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EVALUATION OF TWO-STAGE CATALYTIC

Final Report

by

A. E. Silva

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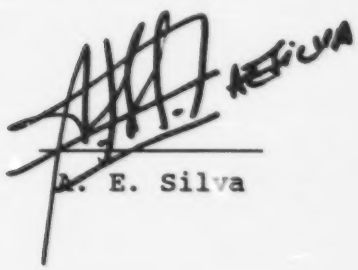

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Microreactor tests were performed by R.K. Lennox, J. Chmielowiec and N. Whitelegg. A. Mahay was responsible for performing high severity tests and pilot plant reactor tests. I.P. Fisher made the kinetic treatment of microreactor tests. Analytical services were supplied by L.W. Beauchamp, J. Thomson, M.H. Vandal and R.J. Bernais. Engine tests were conducted by W. Honchar and M. Marshall. A. Mahay handled the overall interpretation of the results obtained. J. Chmielowiec, then A.E. Silva was Project Manager for this program.

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1. SUMMARY

The objective of this project was to evaluate two-stage catalytic hydroprocessing of nitrogen-containing feeds as a route for increasing product yields and improving product quality. Syncrude gas oil was denitrogenated by catalytic hydrotreating and then hydrocracked in a second stage.

Performance of 3 catalysts: a proprietary catalyst "A", Shell 411 and Shell 753, were evaluated in a microreactor under different operating conditions. Product properties were determined, hydrocarbon composition analyzed, and kinetic modelling was accomplished. In addition, production runs were performed with catalyst "A", using a 1-litre pilot plant reactor.

At temperatures under 395°C, nitrogen compounds in the feed inhibit gas oil conversion to lighter compounds. Extent of the inhibition depends on the N levels in the feed and the catalyst used.

Under those operating conditions, conversions are low and no significant yield enhancement due to denitrogenation is observed, except for Shell 753. This zeolite-based catalyst displays high conversion, together with very high selectivity to naphtha, when the feed is denitrogenated. Catalyst "A", the most affected by nitrogen compounds because of its poorer HDN activity, is also the catalyst which, at higher severity (415°C), benefits the most from feed prehydrotreating.

At higher severity (400-415°C), denitrogenation of the Syncrude gas oil significantly improves naphtha and distillate yields with catalyst "A". An optimal severity (about 408°C/0.5 LHSV, 85% conversion) is observed for distillate yields. Quality of the products when derived from the raw Syncrude gas oil is excellent, and even better when the feed is denitrogenated.

Finally, results suggest that some irreversible catalyst inhibition occurs when the catalyst is exposed to feeds with high nitrogen levels.

1. RESUMÉ

L'objectif de ce projet était d'évaluer le procédé d'hydrocraquage en deux-étapes de charges gasole contenant des composés azotés, comme moyen d'augmenter les quantités produites et d'améliorer la qualité des produits. Un gasole Syncrude fut dénitrifié par hydroraffinage, puis hydrocraqué en une deuxième étape.

La performance de trois catalyseurs (un catalyseur "A", Shell 411 et Shell 753) fut evaluée à l'aide d'un microréacteur sous une grande gamme des conditions opératoires. Les propriétés des produits furent determinées, leur composition en hydrocarbures analysée et des modèles cinétiques furent développés. De plus, des essais en mode production furent réalisés avec le catalyseur "A" à l'aide d'un réacteur pilote d' 1 litre.

A des températures inférieures à 395°C, les composés azotés de l'alimentation inhibent la conversion du gasole en produits plus légers. Le degré de cette inhibition dépend du niveau d'azote dans l'alimentation et du catalyseur testé.

A ces conditions d'opération, les conversions sont faibles et aucune augmentation significative des quantités produites suite à le dénitrification du gas oil alimenté n'est observée, à l'exception du catalyseur Shell 753. Ce catalyseur, à base de zéolite, achève des conversions élevées avec une sélectivité très élevée envers la coupe naphta quand l'alimentation à été hydrotraitée préalablement. Le catalyseur "A", le plus affecté par les composés azotés parmi les catalyseurs étudiés, en raison de sa pauvre performance en HDN, est aussi celui qui, sous des conditions d'opération plus sévères (415°C), bénéficie le plus de l'hydrodénitrification.

Des essais, conduits dans des conditions plus sévères (400-415°C) avec le catalyseur "A", démontrent que la dénitrification du gasole Syncrude améliore grandement la production de naphtha et distillat moyen. Une production optimale de distillat moyen a lieu à une certaine severité d'opération (408°C/0.5 LHSV) avec l'alimention dénitrifiée. La qualité des produits dérivés du gasole non traité est excellente et encore meilleure quand l'alimentation est hydroraffinée dans une première étape.

Finalement, les résultats suggèrent qu' une inhibition, irréversible dans une certaine mesure, du catalyseur a lieu quand celui-ci est exposé à des alimentations avec un taux d'azote élevé.

2. INTRODUCTION

2.1 Objective

The overall objective of this project is to evaluate two-stage catalytic hydroprocessing of nitrogen-containing feeds as a route for increasing product yields and improving product quality.

The specific objectives are as follows:

- to examine the effect of feedstock nitrogen content on hydrocracking Syncrude gas oils in terms of:
  - volumes and reforming capabilities of the hydrocracker naphtha
  - volumes and cetane quality of the middle distillate

- to interface the hydrocracker product with the total refinery product slate by:
  - increasing the total gasoline pool (volume and octane quality)
  - enhancing the total diesel fuel pool (primarily in terms of cetane quality and exhaust emissions)

- to provide data to investigate future trends concerning Diesel Desulfurization capacity in view of anticipated diesel fuel legislation with respect to exhaust emission particulates.

2.2 Justification

As reserves and production of light and medium conventional crude oil in Western Canada are declining, synthetic crude oil production is expected to grow in the next decade [1]. Predictions estimate that the production of Synthetic Crude Oil will double at the end of the century. Recent months have seen the start-up of a heavy oil upgrader in Regina, Sask. and completion of a capacity addition of Syncrude in Fort McMurray, Alta. The OSLO project, scheduled for 1997, though based on a different upgrading concept (hydrogen addition instead of carbon rejection), will also increase the synthetic oil production. In response to the penetration of synthetic crude into the Canadian crude supply, several synthetic crude specific units have been installed in refineries: Petro-Canada Edmonton, Shell Scotford, Esso Strathcona. These alternative feeds are heavier, more aromatic and contain more nitrogen than conventional feeds. As a consequence, they require more severe processing.

In conjunction with the increased production of synthetic crude oil, a more stringent legislation with respect to exhaust emissions from transportation fuels and lead phase-out is anticipated for the coming years.

Those two factors, in combination with encouraging results from a previous study [2], have motivated the study reported here, with the objective to advance observed relationships and provide data to investigate the effect of the increased hydrogen pretreatment capacity on the total refinery product slate.

2.3 Background

Synthetic crudes, commercially developed at Syncrude Canada Ltd., have specific characteristics that make them unique. They are a bottomless blend of hydrotreated naphtha and gas oil derived from fluid coked bitumen. They also include a high aromaticity and low sulfur content. Analyses of the gas oil fraction of the synthetic crude oil have revealed high content of NH-type species and higher ratios of pyrrolytic nitrogen to basic nitrogen in comparison to conventional gas oil [3].

The adverse effects of nitrogen compounds on catalyst activity, processability and product quality in hydrocracking have been reviewed in a former report [2].

Hydrodenitrogenation (HDN) is the catalytic process by which an organic nitrogen compound is converted to hydrocarbons and ammonia in the presence of hydrogen. In petroleum refining operations, HDN is performed at temperatures ranging from 350 to 420°C and pressures involving several thousand psi of hydrogen. Heterogeneous catalysts (Ni-Mo, Co-Mo and Ni-W) are usually employed. Nitrogen is removed as ammonia both to eliminate potential poisons for downstream refinery catalysts and to render resultant fuel products more environmentally acceptable (NO_x emissions).

HDN proceeds via saturation (hydrogenation) of the ring followed by hydrogenolysis of the C-N bonds, first to open the hetero-ring and then to convert the resulting aliphatic or aromatic amine intermediates to hydrocarbon and ammonia. C-N bond breakage rather than ring hydrogenation is generally rate determining. However, steric hinderance can render hydrogenation of bulky molecules difficult [4]. Also, hydrodenitrogenation is usually slower than hydrodesulfurization.

HDN activity of hydrocracking catalysts depends on the level of denitrogenation, the type of nitrogen compounds present in the

feed and operating conditions. However, Ni-based catalysts are generally more effective for N removal than Co-based catalysts [4]. A study of catalytic hydrocracking of heavy gas oil (5600 ppm N) has shown that at high nitrogen content, Ni-W/Al was the best for cracking, hydrogenation and HDN, when compared to Ni-Mo/Al and Co-Mo/Al [5].

The previous study mentioned earlier [2] specifically looked at the effect of the total level and the type of nitrogen compounds on the hydrocracking of Syncrude Gas Oil. In these experiments, denitrogenated feed was prepared by two-stage extraction of nitrogeneous compounds. Model compounds were then added to the denitrogenated Syncrude Gas Oil up to the initial nitrogen level to study the influence of the type of nitrogen. The hydrocracking catalysts were Ni-W supported on amorphous silica-alumina or zeolite compounds. The conclusions were as follows:

- At hydrocracking temperature range nitrogen components (presumably converted to ammonia) appear to block reversibly active surface sites;

- Nitrogen compounds inhibit cracking and aromatic ring saturation reactions;

- Gas oil conversion to light products is affected by the total nitrogen content of the hydrotreated feed. Nitrogen functional groups appear to change characteristics of the total liquid product to a small degree.

- Denitrogenation enhances naphtha and middle distillate yields. The yield enhancement is a function of hydrocracking severity;

- Hydrocracking of denitrogenated SGO yields light and heavy distillates of higher cetane number than those derived from raw SGO;

- Octane blending values appear to be higher for naphtha of DSGO origin.

In one experiment, nitrogen-extracted feed was replaced by a catalytically denitrogenated feed. At 390°C, the catalytically treated SGO yielded the same naphtha volume, but more middle distillate product. It was then natural to conduct a similar study to evaluate the potential of a two-stage hydrocracking process with a mild catalytic hydrogenation substituting solvent extraction prior to hydrocracking.

3. EXPERIMENTAL

3.1 Feed Preparation

Syncrude Gas Oil (SGO) obtained from Petro-Canada's Edmonton refinery was employed in this study.

420 litres of denitrogenated SGO (DSGO) was produced by hydrotreating SGO in a 2 L reactor over Shell-424 catalyst. The operating conditions were: 1500 psi, LHSV = 1.0 h^{-1} and the bed temperature was adjusted at 375°C to achieve 75% denitrogenation. The reactor liquid effluent was nitrogen purged and later washed to remove ammonium sulfide.

Then, the initial boiling point of both feeds, SGO and DSGO, was adjusted to 315°C by distillation in a 200 L Mark II fractionator. The results of the fractionation are given in Table 1.

Finally, the two 315°C+ feeds were characterized by simulated distillation (GCD), mass spectrometry and analyzed for sulfur and nitrogen. Results are tabulated in Table 2.

3.2 Catalysts

Three catalysts were used in this study. These are:

- Shell 411 (Ni = 3%, Mo = 22%)
- Proprietary hydrocracking catalyst "A" (Ni = 20%, W = 20%)
- Shell 753 (Zeolite-based hydrocracking catalyst).

The Shell 411 and Shell 753 samples were supplied by Shell Chemical Company.

The microreactor tests employed ground, sized to 0.6-1 mm (8-16 mesh) particles. Catalyst "A" was used as received, i.e. 1/16" extrudates, in the pilot reactor test.

3.3 Microreactor Tests

3.3.1 Apparatus

The continuous flow, in-house constructed reactor system, shown in Figure 1, was used in this study. The liquid is fed by gravity from a 250 mL burette to a Waters model 510 pump which can be set to maintain a constant flow at, typically, 3000 psi. Hydrogen is introduced at a constant pressure. The reactor is operated in the down-flow mode.

The reactor is a 316 SS 3/4 in. (19.1 mm) O.D. x 0.44 in. (11.1 mm) I.D. Autoclave Assembly CL294SS20 with a maximum pressure rating of 20 000 psi at 72°F.

The reactor, along with a preheat coil and mixing coil, is maintained inside a specially built oven. The oven is constantly purged with nitrogen and an internal blower distributes heat evenly to all parts of the oven.

The nominal bed size is approximately 30 mL. In this study, a 15 mL undiluted bed was used. It was supported by a layer (1 mm) of glass wool.

A Tescom 44-2020 back pressure regulator was used to maintain the required pressure in the system. The product stream passed through a two-stage receiver system, where liquid-gas separation took place. Off-gases passed through a gas sampling orsat, a wet test meter and then to vent.

3.3.2 Operating Procedure

In obtaining experimental data on catalytic hydrocracking, considerable attention was necessary to ensure constant reaction conditions, mass balancing and sample integrity. Therefore, stabilization of reactor pressures and temperatures as well as feed charge and product flow rates were monitored. In addition, a level of the catalyst activity was monitored by measuring density of the liquid effluent in four-hour increments.

For the microreactor runs involving fresh catalyst, the following procedure was developed:

1. The reactor tube was loaded with the catalyst and sealed.

2. The catalyst was dehydrated at 190°C under nitrogen over 24 hours.

3. The reactor was then pressure tested at 20.7 MPa for 24 hours.

4. With catalyst "A" and Shell 411, the catalyst was soaked by starting the liquid feed (hydrotreated base oil) with the ractor pressure maintained at 20.7 MPa. Hydrogen flow was controlled in such a way that H_2/Feed oil ratio was kept at 900 L/L gas oil (5000 SCFB).

5. The reactor was heated up to 260°C at 3°C/min.

Then followed the presulfiding step.

6. For catalyst "A" and Shell 411, the feed was replaced by the same base oil spiked with dimethyldisulfide (DMDS) to the equivalent of 6000 ppm sulfur. The gas rate is still at 900 L/L of gas oil with a minimum of 93% H_2 composition.

   Presulfiding was carried out at 2750 psig pressure and 0.5 LHSV and their conditions were maintained until the prescribed amount of sulfur had been passed over the catalyst. Each H_2S breakthrough was followed by a temperature increase of 30°C until 420°C was reached.

   The H_2S concentration in the effluent was monitored for two hours after the final breakthrough to ensure sulfiding was complete.

   Presulfiding typically takes 48 hours.

   For Shell 753, the wet sulfiding method is not recommended, because of possible coking of the catalyst which will lower its initial activity. A staged gas phase presulfiding method was more appropriate. The sulfiding was on 10% H_2S in H_2 mixture. Operating pressure was 25 atm. After establishing the gas flow and pressure, the reactor was brought to 135°C and maintained at this temperature for 2 hours. Then the temperature was successively set to 210, 260, 310 and 370°C, each temperature being maintained for 45 minutes. Time for each temperature increase was typically 15 minutes. The final temperature, 370°C, was kept for a minimum of 1 hour before reducing it to 150°C while maintaining the gas flow.

7. The feed was then switched to the Syncrude Gas Oil 315°C+ and the conditions (temperature and space velocity) set at the selected values:

   Kinetic Study: High Nitrogen SGO feed, 395°C, LHSV = 2
   High Severity Study: Low N DSGO feed, 400°C, LHSV = 1.0

   In the case of catalyst Shell 753, special care was taken when admitting the feed (SGO). After establishing hydrogen flow rate and pressure, the feed was admitted with the reactor at 150°C. Then the temperature was increased by 25-30°C steps, each temperature being maintained for 1 hour. The system was lined-out at 260°C for 14-20 hours before slowly setting the temperature selected for the first run (395°C).

Initial catalyst activity decreased steadily until an equilibrium between the presulfided catalyst and sulfur content of the feed was reached. This was considered to be the steady-state catalytic activity and it usually required several days to develop.

8. Samples of liquid product were drained at 4 h intervals, while temperatures, pressures and feed flow rate were recorded. The liquid product rate was determined by weighing drained liquid effluent samples.

9. Samples submitted for sulfur and nitrogen analyses were washed twice with equal amounts of 15% w/v cadmium sulphate acidified with 0.4N sulfuric acid followed by three separate water washes to remove residual cadmium sulfide and ammonium salts.

10. The run was carried on until sufficient liquid volume (200 mL) was collected for fractionation. A gas sample was also taken at the end of the run for mass balancing.

11. Temperature and/or space velocity were then set to the next conditions and the sampling procedure was repeated after a new steady-state was reached, usually at a much faster rate than in the initial run.

3.3.3 Product Analyses

Nitrogen and sulfur levels were measured in purged and washed liquid samples. Liquid products were fractionated into 4 fractions (Kinetic runs) or 3 fractions (high severity tests). Each fraction was then analyzed for its hydrocarbon composition by mass spectrometry. Finally, hydrogen consumption was derived from the hydrocarbon composition and yield data.

3.4 Pilot Reactor Tests

3.4.1 Description of Pilot Plant Reactor

The XYTEL Hydrotreater pilot unit (Fig.2) consists of a 5-foot (150 cm) reactor tube, feed pump, electric preheater, liquid-gas separator, product cooler, pressure regulators and a wet test meter.

The reactor 1.5 in. (3.80 cm) I.D. tube was filled with 10 cm of ceramic beads on top, followed by 103 cm or 800 mL (756 g) of catalyst bed and another 37 cm of ceramic beads at the bottom. The thermowell contains 10 thermocouples equally distributed along the reactor length. Heaters are controlled in such a way

that the reactor is operated in an isothermal mode. Temperature deviation from the average bed value (ABT) did not exceed 2°C.

The oil was pumped from a feed tank to the top of the reactor while H_2 was simultaneously fed concurrently from a pressure regulator. The product at the exit of the reactor was cooled down in a condenser, then gas and liquid were separated in a high pressure separator, from which the hydroprocessed liquid flowed into a product reservoir, where it was drained regularly and weighed for mass balance. The gas from the separator was depressurized through a control valve then passed into a knock-out pot and out to the vent through a wet test meter. The gas was sampled with an orsat before the wet test meter.

3.4.2 Operating Procedure

The procedure used for the microreactor tests was also followed for the production runs. The catalyst was de-edged with a Syncrude oil feedstock.

3.5 Particulates in Exhaust Emission Measurement

The engine used for this test was a single-cylinder direct injection diesel engine (Lister, England). All samples were taken on diluted exhaust using a mini-dilution tunnel. Dilution ratio, calculated from CO_2 concentration in diluted and undiluted exhaust stream was 6 to 7. Engine power output was 2.88 kW (3.9 HP).

Equivalence ratio (actual fuel-air ratio divided by stoichiometric fuel-air ratio) was close to 0.20.

The dilution tunnel was built according to the specification of reference 7. Methodology described in [7] for sampling collection and handling was followed as well.

4. RESULTS

4.1 Microreactor Tests - Kinetic Study

Fourteen (14) hydrocracking experiments were performed on each catalyst and each feed, for a total of 24 runs per catalyst. The same catalyst bed was used for the 24 runs. They were carried out under a combination of the following operating conditions:

4 Temperatures (°C)	x	3 LHSV (h^{-1})
360		0.5
370		1.0
383		2.0
395		

An extra run at 415°C, 1 LHSV was also carried out. The total pressure was held constant at 2750 psi (18.7 MPa) for those runs. Pressure effect was studied by conducting an additional run at 370°C, 1.0 LHSV and 1500 psig. In the case of Shell 753, the runs at 360°C were not performed.

Run sequence for each catalyst is given in Appendix B. Runs with SGO feed were always carried out first.

Also, two additional runs with NH_3 spiked denitrogenated feed (1494 ppm Nitrogen) were carried out on catalyst "A" at 395°C, 1 LHSV and 383°C, 1 LHSV, both under a 2750 psi hydrogen pressure.

Operating conditions and results such as nitrogen and sulfur levels in the liquid product, hydrogen consumption, mass balance and hydrocarbon composition of each fraction, are gathered in Tables 3 to 8 for each catalyst and each feed tested.

Runs carried out at 360°C are not reported in those tables, no significant gas oil conversion having been observed. However, Nitrogen and Sulfur levels in the reactor liquid effluent can be found in Appendix A.

Some runs conducted on Shell 753 Zeolite-based catalyst with the denitrogenated feed were not reported because of poor mass balancing and the difficulty of obtaining liquid products with stable quality (density). Also, the first three runs on Shell 753 (SGO feed, LHSV = 2.0 h^{-1}) were repeated, de-edging of the catalyst having been judged not fully achieved prior to those runs.

4.2 Microreactor Tests - High Severity Runs

Nine runs were carried out on a sample of catalyst "A" with each feed, the raw SGO and the denitrogenated SGO, under 2750 psi pressure and with a 5000 SCFB (890 L/L) H_2/Feed ratio. Temperature and space velocities for each run were set at a combination of the following values:

Temperature (°C)	x	LHSV (h^{-1})
400		0.25
408		0.5
415		1.0

Operating conditions, mass and volume product yields, inspections and hydrocarbon composition of the liquid product for each of the 18 runs are compiled in Tables 9A and 9B. Runs are chronologically numbered.

4.3 Production Runs in Pilot Reactor

Three consecutive production runs, using three different feeds, were performed on catalyst "A" under fixed operating conditions: 2750 psi (18.7 MPa) pressure, 408°C temperature, 0.5 h^{-1} LHSV and 5000 SCFB (890 L/L) H_2/Feed ratio. The three feeds were processed, starting from the lowest Nitrogen level SGO, in the following order:

- 100% vol. Denitrogenated Syncrude Gas Oil (DSGO) 315°c+
- 70/30 vol.% DSGO/SGO
- 100% Syncrude Gas Oil (SGO) 315°C+

The goal was to produce about 100 litres of total liquid product from each feed, in order to obtain a volume sufficient to conduct the particulate exhaust emission test in our Engine Test Lab.

The total liquid product was fractionated in a 200 litre Mark II fractionator, equipped with a 15 theoretical plate packed column, which provides sharp cuts of the distilled fractions.

Mass balances and volume yields for the three runs are gathered in Table 11. Various inspections and hydrocarbon analyses of naphtha, light- and heavy-distillates and gas oil 315°C+ are listed respectively in Tables 12, 13, 14 and 15.

5. DISCUSSION

5.1 Feed Compositions

Raw and denitrogenated feeds were analyzed to examine compositional differences (Table 2). The hydrotreatment of the Syncrude gas oil has resulted in some conversion of the 315°C+ fraction into lighter hydrocarbons: the 315°C+ hydrotreated fraction is 96.2 wt.% (98.1 vol.%) of the original 315°C+ fraction (Table 1).

Not only the nitrogen content has been reduced (by 76%), but sulfur content has been substantially lowered too (by 91%).

The hydrodenitrogenation and hydrodesulfurization has also been accompanied by significant aromatic ring saturation as indicated by the hydrocarbon analysis. We mostly observe an increase of cycloparaffins at the expense of polyaromatic hydrocarbons.

5.2 Microreactor Tests - Kinetic Study

5.2.1 Qualitative Evaluation of Catalyst Performances

SGO hydrotreating effects on the yields and quality of the products from hydrocracking with catalyst "A", Shell 411 and Shell 753 are illustrated in Figures 3 to 15 (cat. "A"), Figures 16 to 28 (Shell 411) and Figures 29 to 41 (Shell 753).

Catalyst A

On catalyst "A", at severity 395°C/0.5 LHSV and lower, 315°C+ gas oil conversions were low (<10 wt.%) and were not significantly different, whether the feed was the raw or denitrogenated SGO. Practically no naphtha was formed. At higher severity, the beneficial effect of pretreating the feed started to show up, higher conversions having been recorded when DSGO was the feed. Those observations mean that the level of nitrogen achieved after pretreatment of the Syncrude gas oil was still too high to have a positive effect in the second stage of the process, at 395°C and lower temperatures. In this range of temperatures, nitrogen compounds were strongly absorbed on the catalyst surface, and inhibited hydrogenation and cracking activity. At higher temperatures, notably 415°C, those poisonous compounds were more readily eliminated and/or less strongly absorbed and, as a consequence, higher conversions were observed.

Catalyst Shell 411

On Shell 411, hydrogen consumptions (Tables 3-4 and 5-6) and nitrogen content in total liquid product (Fig. 5 and 18) reveal

more extensive hydrogenation and HDN activity, as compared to catalyst "A".

Gas oil conversions, while low (less than 15 wt.%), were surprisingly higher with the raw feed than with the denitrogenated SGO. The reason is the different degree of hydrogen saturation of the two feeds. Hydrogenation, a relatively facile reaction, is not significantly affected by the nitrogen level in the feed, due to the good HDN activity of Shell 411. The raw feed being less hydrogenated, more hydrogenation occurred with this feed, as shown by hydrogen consumption numbers (see Tables 5 and 6). In addition, hydrogen saturation of the raw feed was accompanied by some conversion (≈4.0 wt.%) into lighter products, as it was reported in the feed preparation. The result was a slightly higher conversion of the raw SGO feed.

If the level of nitrogen in the feed had no significant effect on the hydrogenation activity of Shell 411, conversion remained low with both feeds at temperatures under 395°C, indicating no significant cracking activity. Nitrogen levels achieved within the catalyst bed were still sufficient to poison most of the Shell 411 acid sites, responsible for cracking.

At those low gas oil conversions, higher aromatic and paraffin contents were observed in the distillates from the denitrogenated feed. Two explanations can be proposed. First, the slight gas oil conversion accompanying the gas oil hydrotreating mentioned above has produced mostly cycloparaffins. They were eliminated from the pretreated feed when its initial boiling point was adjusted to 315°C. On the other hand, when the feed contained less nitrogen compounds, some cracking has contributed to a small degree to the 315°C+ gas oil conversion, in such a way that polyaromatics present in the gas oil feed were dealkylated before being fully hydrogenated into polycycloparaffins. The products of this paring reaction were lighter aromatics and paraffins in the distillate range, resulting in a higher aromatic content in distillate cuts with the DSGO as feed.

At higher severity (415°C), no yield enhancement was observed with Shell 411, most nitrogen having been removed whatever was the initial nitrogen content in the feed. On the contrary, with catalyst "A", yield was clearly enhanced at 415°C, when Nitrogen level in the gas oil feed was lowered. Actually, at 415°C/1 LHSV, conditions at which denitrogenation was almost complete on both catalysts, DSGO conversion was higher on catalyst "A" than on Shell 411 (Figures 3 and 16). Also, hydrogen consumption was higher, suggesting that the higher hydrogen consumption on Shell 411, as compared to catalyst "A", observed at lower severity, was

not the result of an intrinsically higher hydrogenation activity of Shell 411. It was rather due to a stronger inhibition of the hydrogenation sites of catalyst "A", by strong adsorption by nitrogen compounds, as a consequence of its lower HDN activity.

Hydrotreating of the Syncrude gas oil feed to decrease nitrogen content has no beneficial effect when Shell 411 is the hydrocracking catalyst employed, mostly because of its good HDN activity. Activity of catalyst "A", not as good a HDN catalyst as Shell 411, is more affected by the nitrogen level in the feed. However, the level of denitrogenation reached in the DSGO feed was not sufficient to enhance hydrocracking activity under the range of operating conditions studied. Higher denitrogenation levels or a higher severity (as shown by the experiment at 415°C) would be required to see a significant yield enhancement. This observation motivated an extension of this study by conducting runs at higher temperatures.

Catalyst Shell 753

On Shell 753, the zeolite-based catalyst, the effects observed with Shell 411 were even more pronounced: deeper denitrogenation, more extensive hydrogenation based on hydrogen consumption, and significant conversion to lighter products. However, pretreatment of the feed resulted in higher gas oil conversion, indicating that nitrogen level still affected the extent of the conversion. Under high severity operating conditions (low space velocity and/or high temperature), 100% gas oil conversion was achieved with the low nitrogen feed. High selectivity to naphtha was observed, reaching 90% at high conversion. In any case, heavy distillate yields were very low. This product yield structure reveals a strong cracking function as compared to the hydrogenation function of Shell 753.

Experiments conducted on catalyst "A" with NH_3 spiked denitrogenated feed indicated no significant effect on the total gas oil conversion (Table 3). However, conversions were low and, in addition, the kinetic study presented in the following section has shown that the Nitrogen level did not influence the reactivity of the Syncrude gas oil on catalyst "A" at low severity. As a consequence, those results are not really meaningful, regarding how ammonia released by the HDN reaction affects the cracking activity of the catalyst.

5.2.2 Kinetic Study

One of the objectives of this project was to examine the pseudo-kinetics of denitrogenation, desulfurization, aromatics hydrogenation and gas oil conversion.

The kinetic treatment of data obtained with Shell 753 was not done because of the high conversion levels reached and the lack of reliable data for some runs.

All the details of this kinetic study, including rate equations, are reported in Appendix A. Here follows the most important findings:

- Catalyst "A" was lower in activity in all respects (conversion of S, N, aromatics and gas oil) than Shell 411.

- Pseudo-kinetics for sulfur and nitrogen removal were found to be first order. However, to rationalize data on Shell 411 with the raw SGO feed, a distinction between reactive and unreactive sulfur (270 ppm) was needed.

- Nitrogen removal rates from the raw SGO with Shell 411 were higher than sulfur removal rates, and also than N removal rates from the denitrogenated feed.

- Catalyst "A" exhibited about half the activity of Shell 411 for both feedstocks, and kinetic parameters are barely affected by the N level in the feed. From activation energy values, Shell 411 is less temperature dependent than Catalyst "A".

- The kinetic values confirmed that, on Shell 411, the more aromatic raw Syncrude gas oil underwent hydrogenation more readily than the denitrogenated gas oil. Both feedstocks behaved similarly towards cracking. On the contrary, there were indications that catalyst "A", at higher temperatures (415°C), found the denitrogenated gas oil easier to crack than the raw Syncrude gas oil. Also, aromatics were more easily saturated at 415°C with the denitrogenated feed as compared to the raw SGO. At lower severities, no significant differences were observed between the two feedstocks.

- Under the range of conversions studied, a correlation between conversions and yields of gas + naphtha and yields of distillates, valid with both catalysts and both feedstocks, was found: distillate yield and gas + naphtha yield were respectively two-thirds and one-third of the conversion.

5.3 High Severity Tests

Catalyst "A" was chosen for the yield enhancement study because of its higher sensitivity to the nitrogen level in the feed at high severity, as revealed by the kinetic study, notably the run at 415°C.

Yields and properties of the liquid product fractions from both feeds are compared in Figures 42 to 50.

5.3.1 Qualitative Evaluation

There was a clear yield enhancement as a result of hydrotreating the Syncrude Gas Oil in a first step:

- overall gas oil conversion increases (Fig. 46) reached close to 50 vol.%. on an absolute basis.

- naphtha yield enhancement (Fig. 44) varied from 75 to 35 vol.% absolute in the whole range studied.

- distillate production (Fig. 45) from the denitrogenated feed went through a maximum at 408°C/0.5 LHSV. When severity was increased above this point, distillate yields started to decrease. At 415°C/0.5 LHSV and higher severities, distillates from the raw SGO feed were produced in higher yields.

Reformer quality (Fig. 47) of the naphtha cut, based on its N+2A (Naphthene + 2 x Aromatic, vol.%) value, did not vary in great extent and remained between 65 and 75 vol.%. It tended to decrease with increased conversions. In most cases, quality of the naphtha derived from the raw SGO feed was higher, as a result of less hydrogenation of the aromatics. However, differences were small and at 408°C/0.5 LHSV, N+2A values of reformer feedstock produced from both feeds were very close (72-73). At higher severity, naphtha quality from the denitrogenated feed decreased, while it remained fairly constant when the naphtha originated from the raw 315°C+ SGO.

Distillate quality (Figures 48-50) as a jet fuel/diesel feedstock was improved when the feed was hydrotreated before hydrocracking. Aromatic content was substantially lowered due to the deeper hydrogenation. It stayed under 20 vol.%, while aromatics in distillates derived from the raw SGO varied between 40 and 28 vol.%, which is not acceptable for Jet A fuel specifications (max. 20 vol.%). Paraffin content decreased at severity above 415°C/1.0 LHSV.

As the temperature was increased from 408 to 415°C, aromatics in the distillate produced at low space velocity (0.25 LHSV) increased. The thermodynamically unfavoured reversible aromatic saturation at higher temperatures contributes to this phenomenon.

Effects of the pretreatment of the Syncrude gas oil on the hydrocracking performance of catalyst "A" are assessed from a different angle in Figure 51 and Table 10. In Figure 51, effect of the 315°C+ gas oil conversion on the naphtha and distillate yields is depicted for both SGO and DSGO feeds. A clear optimum for distillate yields is observed at 85% conversion, when the feed is DSGO. No data were obtained at higher conversions with SGO as the feed. However, the distillate yields levelled off when the conversion approaches 85%. We expect that it would eventually drop beyond this conversion level, as is observed with the DSGO feed. Figure 51 also shows that distillate selectivity was fairly constant up 70% conversion with the raw SGO feed. Above this point, naphtha selectivity increased. On the other hand, when the feed was pretreated, naphtha selectivity monotonically raised with conversion up to 90% conversion, beyond which it increased dramatically as a result of distillate overcracking.

Product yields and qualities from SGO and DSGO are compared at two levels of conversion, 60 and 85 wt.%, in Table 10. To achieve the same conversion, SGO hydrocracking required higher temperature (about 15°C). Product selectivity was also affected by the feed pretreatment. At fixed conversion, SGO hydrotreating enhanced the naphtha yields, as a result of a lesser degree of poisoning by nitrogen compounds of the acid sites, responsible for the cracking activity of the catalyst. This was also observed at higher severity (85% conversion) even if very low nitrogen levels in the total liquid products were achieved, in the case of the SGO feed.

At both levels of conversion, naphtha quality as a reformer feedstock, measured by its N+2A value, was barely affected. However, naphtha from the DSGO feed was more naphthenic due to a higher degree of aromatic saturation. At high severity (85% conv.), the lower N+2A value of the naphtha derived from the DSGO feed was the result of a higher degree of aromatic saturation and cracking to paraffins.

Distillate quality was clearly improved by the pretreatment of the gas oil feed, at both levels of conversion, as shown by the aromatic content.

Finally, the following observation must be mentioned. Conversion of the denitrogenated SGO at 415°C/1.0 LHSV in the high severity test was much higher (91 wt%) than the one recorded in the previous set of runs, on catalyst "A" (46 wt%). On the opposite, raw SGO conversions were close (42 and 46 wt%). The major difference between the two series of runs was that the low severity

tests were carried out by first conducting all the runs with the high N raw SGO feed, then the runs with the denitrogenated SGO. The opposite sequence was followed in the high severity series of tests. This suggests that strongly adsorbed Nitrogen compounds do not readily desorb, and irreversibly poison to a certain extent the catalyst surface, even when the catalyst is later exposed to a feed with a lower Nitrogen level, at the same operating conditions. Higher temperatures may be required to desorb and/or convert those strongly adsorbed N compounds.

5.3.2 Kinetic Study

5.3.2.1 Gas Oil Conversion

In the previous study, results were found to be satisfactorily fitted with a first-order kinetic rate model. However, in the present case, this is not true anymore. Over a wide range of conversions, second-order kinetics provide a better yield prediction with both gas oil feeds, as shown in Table 16.

Nevertheless, when first-order k values computed for the runs with the raw SGO were reported in an Arrhenius plot (Log k vs 1/T), they fairly well obeyed the Arrhenius law, when grouped by space velocity (see Fig.52). However, E, the activation energy, dropped from 75-80 kcal/mole at 1 and 2 h contact time to about 50 kcal/mole at high contact time of 4 h. Three different explanations can be put forward:

Variation in Gas Oil Component Reactivity

As mentioned earlier, first-order kinetics does not predict well conversions on a wide range of conversions, because lumping gas oil compounds in a single entity is not adequate anymore. At high operating severity (high contact time), high conversions are reached and more refractory material must be cracked. Usually, low activation energy is associated with low reactivity. This could explain the drop in activation energy observed at high conversion (high contact time).

Diffusional Effect

For first-order rate equation, diffusional effect increases with

Thiele modulus, $\phi = L\sqrt{k_v/D_e}$ where:

L = distance from center to surface of catalyst pellet (m)
k_v = 1st-order rate kinetic constant (h^{-1})
D_e = effective diffusivity ($m^3/m.h$)

[6]. At high conversions, nitrogen and sulfur levels in the catalyst bed are low and their inhibition effects brought down. As a result, the kinetic rate constant k_v, then $\emptyset$, increases to such a point that the reaction takes place in the diffusion controlled regime, under which the apparent activation energy is half the value measured when the reaction is free of transportation limitations.

Nitrogen (and Sulfur) Inhibition Effects

If heteroatom compounds are strong inhibitors of the gas oil conversion, the kinetic expression should be:

$$d\,[315°C+] / dt = k\,[315°C+] / (1 + K\,[S,N])$$

where [315°C+] and [S,N] are the concentrations in the reaction medium of respectively gas oil and heteroatom [S,N] compounds. At high sulfur and nitrogen levels, K [S,N] >>1, so that the rate can be approximated by:

$$d\,[315°C+] / dt = (k/K)\,[315°C+]/[S,N]$$

Apparent activation energy is then:

$E_{app} = E_{act} + \lambda_{S,N}$ where $\lambda_{S,N}$ is the heat of adsorption of sulfur and nitrogen compounds on the catalyst surface. This relation shows that at higher space velocity (short contact time), where N and S levels are high in the catalyst bed, apparent activation energy increases. To illustrate this interpretation of the variation of activation energy with space velocity, nitrogen and sulfur level ranges are listed below:

LHSV (h^{-1})	E_{app} (kcal/mole)	S (ppm)	N (ppm)
1.0	81	1043-200	395-45
0.5	75	414-46	100-3.0
0.25	52	69-26	5.2-1.1

Reactivities of the different types of hydrocarbon compounds composing the gas oil were also looked at and are compared in Figures 53 to 55 for the raw gas oil feed at the three temperatures studied.

At 400°C the dominant reaction was the hydrogenation of polyaromatics. Their reactivity was much higher, as compared to the other component types (Fig. 53). This could be due either to a

low inherent cracking activity of this catalyst at this temperature or, more probably, to a strong poisoning by Nitrogen compounds of catalyst acid sites, responsible for cracking. At higher temperatures, differences in reactivity were less marked as cracking reactions became more important. Pseudo first-order kinetic parameters for each type of component are compiled in Table 17. When the feed was the denitrogenated SGO, the strong inhibition of cracking reactions was not observed at 400°C (Fig. 56).

A reactivity pattern similar to what has been reported for hydrogen catalytic cracking was observed here, with paraffins being the most refractory components to cracking (besides polyaromatics hydrocarbons which are not hydrogenated in catalytic cracking). The order of reactivity was actually:

Polyaromatic Hyd. (PAH) > Monoaromatic Hyd. (MAH) > Polycycloparaffins (PCP) > Monocycloparaffins (MCP) > Paraffins (Par).

5.3.2.2 Distillate Yield Production

Different kinetic models were tried. The most straightforward is derived from the following two-step mechanism:

$$\text{GO } 315°\text{C+} \xrightarrow{k_1} \text{Middle Distillate} \xrightarrow{k_2} \text{Naphtha + Gas}$$

where rates are pseudo first-order with respect to reactant. The resulting expression for distillate yield Y_D is:

$$Y_D = \frac{100}{(k_2/k_1 - 1)} [\exp(k_1 t) - \exp(k_2 t)]$$

k_1 values determined in first-order rate modelling of gas oil conversions were used. Very poor fitting was obtained with this model.

Other models were tried. A triangular model widely used for catalytic cracking yield prediction was found to provide the best fitting of yield distillates. The model can be depicted in the following way:

GO: 315°C+ gas oil
D: Distillate (195-315°C)
G: Naphtha + Gas

In such a model, it is assumed that distillates can (over)crack to naphtha and gas and that the hydrocracking of gas oil contributes directly to the production of naphtha + gas.

As in catalytic cracking of FCC feedstock to gasoline, the gas oil cracking rate is second-order:

$$dY_{GO}/dt = (k_1 + k_3)\ Y_{GO}^2 = k_0\ Y_{GO}^2$$

$$dY_D/dt = k_1\ Y_{GO}^2 - k_2\ Y_D$$

$$k_0 = k_1 + k_3$$

k_0 values were calculated above and distillate yields are given by:

$$Y_D = K_1 \left[\exp\left(K_2 - 1/Y_{GO}\right) - Y_{GO} + K_2 \exp\left(-K_2/Y_{GO}\right) \int_{K_2}^{K_2/Y_{GO}} (e^x/x)\ dx\right]$$

where: Y_D and Y_{GO}: weight fraction of distillate and gas oil in products

$K_1 = k_1/k_0$ $\qquad$ $K_2 = k_2/k_0$

$(e^x/x)\ dx$ is a tabulated function

Best estimates for kinetic parameters were calculated using the Marquart non-linear regression algorithm, and are listed in Tables 18 and 19, together with calculated and predicted distillate yields for both feedstocks.

Ratio $K_1 = k_1/k_0$ indicates that 40 to 30% of cracked raw SGO feed was converted directly into naphtha. When the feed was DSGO, gas oil cracking selectivity to distillate was lower (K_1 = 0.45 - 0.55). Besides, while (over)cracking of distillate occurs at high severity and is more important on an absolute basis when the feed is pretreated, kinetics suggest that the distillate/naphtha selectivity is mostly determined by the gas oil cracking step. Indeed, at 415°C $(1-K_1)$, a measure of the importance of direct cracking of gas oil to naphtha, is 0.57 and 0.30 respectively for the DSGO and SGO feeds.

The good adequacy of this model to our data clearly indicates that at high severity, and especially with denitrogenated feed, gas oil hydrocracking occurs in the cracking regime.

5.4 Production Runs in Pilot Reactor

The denitrogenated SGO conversion was somewhat lower (78 wt%) and yield structure different from the one observed under the same operating conditions in the microreactor tests (88 wt% - Table 9/ Run #5). For the raw material, conversions were within expected variance. Again, it is suspected that the de-edging oil used in those production runs contained an amount of nitrogen compounds higher than the denitrogenated SGO (which was used to de-edge the catalyst in the high severity tests). As mentioned earlier, this could have irreversibly poisoned the catalyst, resulting in a lower activity.

Denitrogenation of the SGO means higher conversion, especially where N levels in the feed drop from 780 (run B) to 391 ppm (run A). In the latter case, naphtha yield mostly benefits from the conversion increase (Table 11).

Naphtha quality (Table 12), in terms of octane numbers, is low and barely affected by the N level in the SGO feed. Their paraffins display a high iso-/normal- ratio and, as most of those paraffins appear in the light fraction of the naphtha (less than 85°C), they should be fractionated separately into an excellent straight-run light gasoline. The rest of the naphtha cut should be a high quality reformer feedstock, as indicated by their N+2A value. A lower N level in the SGO feed reduces this N+2A number but the quality remains high (N+2A = 73 for run A). This naphtha, mainly naphthenic, should only require a mild reforming to yield a high octane gasoline blending feedstock.

The results of the middle distillate inspection are given in Tables 13 and 14. The Canadian General Standards Board (CGSB) Specifications for Jet A [9] and Type B Diesel fuels [10] are also indicated in the appropriate tables for reference. Middle distillates produced by hydrocracking of Syncrude gas oil have excellent cetane numbers, well above the usual minimum specification of 40, whatever the N content in the feed. However, the cetane number monotonically increases with the degree of feed denitrogenation. Sulfur levels are very low in all cases. Smoke point specifications for Jet A fuel are met by the light distillates produced from the denitrogenated feeds (runs A and B). Cloud points and pour points make these distillates suitable for very low temperature utilization. The viscosities at -20°C are above the maximum specified for Jet A fuel. This could be offset by blending or changing the selected cut point.

Particulate exhaust emission measurements were done on the total distillate (195-315°C) under fixed experimental conditions.

Results, expressed in the most commonly used units, are given below:

Run #	A	B	C
Feed SGO/DSGO vol/vol	0/100	30/70	100/0
Total Aromatics, wt%	9.9	11.1	16.8
Particulates, g/bHP.h	0.82	0.92	1.00
g/kg fuel	3.1	3.6	3.9

Particulate emissions from diesel engines can vary over a wide range, depending on the engine operating parameters, such as the fuel-air ratio, and on the type of engine utilized for the test [8]. No adjustment of these parameters was attempted to minimize the level of particulate emissions. So, it would be inappropriate to compare the numbers presented here with results from other studies.

Particulate emissions in a diesel engine exhaust are strongly correlated to the fuel end point and its aromatic content [8]. In this study, the distillation range of the fuels tested was identical (195-315°C) and only aromatics content varied as a result of the pretreatment of the gas oil feed. This study shows that a 40% reduction of the aromatics content (from 16.8 to 9.9 wt%) results in an ≈20% reduction of the particulate emission level.

In summary, quality of the distillates, excellent when they are derived from the raw feed, is further improved by hydrotreating of the SGO feed. Those distillates constitute high quality blending stock for jet fuel or diesel pool.

Resid 315°C+ are deeply denitrogenated and hydrogenated whatever the heteroatom content in the SGO feed. This unconverted fraction could easily be recycled to the second-stage hydrocracker.

6. CONCLUSIONS

- At temperatures under 395°C, nitrogen compounds in the feed inhibit gas oil conversion to lighter products. The extent of the inhibition depends on the nitrogen level in the feed and the catalyst used.

- At temperatures of 395°C and less, catalyst "A" hydrogenation activity was the most affected by the N level in the SGO feed. On the contrary, hydrogen ring saturation with Shell catalysts was not greatly inhibited by N in the feed, due to their good HDN activity.

- Cracking activity, and consequently Syncrude gas oil conversions into lighter products, is strongly affected by nitrogen in the feed, especially with catalyst "A" and Shell 411. No significant yield enhancement is observed at temperatures 395°C or less, on those catalysts, when N level in the feed is lowered from 1665 to 390 ppm.

- Shell 753, a zeolite-based catalyst, is the least affected by nitrogen in the feed. Nevertheless, hydrotreatment of the SGO feed results in higher yields and high conversions are attained at 370°C. However, this catalyst displays a high selectivity (above 80%) to naphtha at high conversions.

- Higher severity (400°C+) is required to see substantial light product yields. Catalyst "A" is the catalyst which benefits the most from the hydrotreating of the Syncrude gas oil.

- Under high severity operating conditions, denitrogenation significantly improves naphtha and distillate yields. However, naphtha selectivity is enhanced. The gas oil cracking controls the overall reaction.

- At high severity and with the denitrogenated Syncrude gas oil, an optimal severity (around 408°C/0.5 LHSV, 85% conversion) is observed for distillate yields.

- Product quality, notably for distillates, is generally improved by the first-stage hydrotreatment of Syncrude gas oil, but quality is already excellent with the raw SGO as the feed.

- As a consequence, the main benefit of first-stage mild hydrotreatment of the Syncrude gas oil is yield enhancement or, at fixed conversion, lower hydrocracking reactor temperatures and longer catalyst cycle length.

- Light Naphtha (<85°C) have high iso/normal paraffin ratio and should be high quality straight run light gasoline.

- Naphtha octane is low (≈60) and not affected by N level in the feed. However, naphtha high cycloparaffinicity makes them good reformer feedstock.

- Quality of the distillates, as jet or diesel fuels, is excellent when derived from the raw SGO, and is even better when the feed is denitrogenated.

- Aromatic ring saturation, notably in the middle distillate range, cannot be improved above a certain level by increasing temperature, because of unfavourable thermodynamic equilibrium limitations.

- Irreversible inhibition of the catalyst active sites has been observed when the catalyst is exposed to high nitrogen levels.

7. RECOMMENDATIONS/FUTURE WORK

- If hydrocracking of Syncrude gas oil is set to be carried on at a given nitrogen level in the feed, exposure of the catalyst to feeds with higher nitrogen levels should be avoided.

- Study of the inhibiting effect of nitrogen compounds on catalyst activity should be conducted to clearly establish whether permanent deactivation by strong nitrogen compound adsorption occurs. Methods to restore catalyst activity, such as higher temperature operation, should be evaluated too. Such a study should be complemented by catalyst surface analysis.

- An extension of the present work would be to evaluate whether high light product yields could be achieved at lower reactor temperatures (<400°C) by bringing the nitrogen content in the Syncrude Gas Oil to a level even lower than it was in the present study.

- Catalysts, such as Shell 753, having good HDN and hydrogenation activity, but with a more moderate cracking activity, should be tested to evaluate their potential to offer a good flexibility towards naphtha and distillate yields, without pretreatment of the Syncrude Gas Oil.

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TABLE 1

ADJUSTMENT OF THE INITIAL BOILING POINT OF SYNCRUDE GAS OIL FEEDS

RAW SGO

	Density @ 15°C	wt%	vol%
315°C- overhead	0.8803	11.9	12.6
315°C+ bottom	0.9440	88.1	87.4

DENITROGENATED SGO (DSGO)

	Density @ 15°C	wt%	vol%
315°C- overhead	0.8717	15.2	15.8
315°C+ bottom	0.9263	84.8	84.2

TABLE 2

FEEDSTOCK PROPERTIES
SYNCRUDE GAS OIL 315°c+ (SGO) AND
DENITROGENATED SYNCRUDE GAS OIL 315°C+ (DSGO)

Analysis		
Density @ 15°C, g/mL	0.9440	0.9263
N content, ppm	1665	394
S content, ppm	4100	375
Gas Chromatographic Distillation (GCD), °C		
IBP	286	291
10%	332	329
20%	352	351
30%	370	368
40%	387	384
50%	404	400
60%	421	418
70%	440	436
80%	464	459
90%	496	492
FBP	615	579
Mass Spectrometry, Mass %		
Paraffins	6.82	7.21
Cycloparaffins	35.35	50.10
mono-	8.68	12.99
poly-	26.87	37.11
Monoaromatics	23.75	24.87
Polyaromatics	27.81	15.78
Di-	15.95	11.80
Tri-	7.06	3.35
Tetra-	3.20	0.29
Penta-	1.60	0.34
Sulfuraromatics	3.58	1.52
Others	2.69	0.52

TABLE 3

Cat. A - DENITROGENATED SYNCRUDE GAS-OIL

Run #	1	2	3	4	5	6	7	8	9	10	11	12(NH3)	13(NH3)
REACTION CONDITIONS													
Temperature (oC)	415	395	395	395	383	383	383	370	370	370	370	395	383
LHSV	1.00	0.50	1.00	2.00	0.50	1.00	2.00	0.50	1.00	2.00	1.00	1.00	1.00
Pressure (psi)	2750	2750	2750	2750	2750	2750	2750	2750	2750	2750	1500	2750	2750
H2/Feed (SCFB)	5000	5000	5000	5000	5000	5000	5000	5000	5000	5000	5000	5000	5000
H2 consumption (SCFB)	766	654	253	85	230	133	54	146	36	16	35	271	89
INSPECTION DATA													
total N in TLP (ppm)	0.9	3.0	35.0	139.0	26.0	84.0	203.0	79.0	163.0	221.0	251.0	42.0	97.0
total S in TLP (ppm)	65	18	67	166	25	135	208	104	188	237	238	18	82
total N in 315oC+ Resid (ppm)	2.2	0.5	43.0	126.0	56.0	61.0	213.0	80.2	171.0	209.0	256.0	-	-
total S in 315oC+ Resid (ppm)	8	68	110	193	64	148	253	114	210	257	258	-	-
density @15C liquid product	0.8445	0.8732	0.9011	0.9173	0.9083	0.9131	0.9204	0.9156	0.9198	0.9222	0.9231	0.9064	0.9153
PRODUCT YIELD WT%													
Gas	1.3	1.7	1.3	0.5	1.1	0.5	0.4	0.6	0.2	0.5	0.3	1.3	0.4
Naphtha (IBP-195oC)	20.0	9.0	3.2	0.9	1.5	1.7	0.0	0.0	0.0	0.0	0.0	1.9	0.9
Lt Distillate (195-290oC)	27.0	14.9	3.7	1.6	3.8	3.3	1.2	2.3	0.9	0.5	0.9	5.9	1.9
Hy Distillate (290-315oC)	8.4	7.5	3.0	2.1	3.3	1.5	0.7	2.1	1.1	0.9	0.7	2.3	2.7
Gas-Oil (315oC+)	43.3	66.9	88.8	94.9	90.3	93.0	97.7	95.0	97.8	98.1	98.1	88.6	94.1
NAPHTHA (BP-195oC) Vol%													
Paraffins	36.15	32.74	28.96	30.38	28.64	25.78	-	-	-	-	-	30.09	31.77
Isoparaffins	32.12	27.80	19.00	19.48	19.84	17.35						19.71	22.68
n-paraffins	4.04	4.94	9.96	10.89	8.80	8.43						10.39	9.09
Naphtenes	56.61	60.61	58.50	55.97	61.93	61.41	-	-	-	-	-	59.46	57.17
Aromatics	7.23	6.65	12.54	13.65	9.43	12.81	-	-	-	-	-	10.44	11.06
DISTILLATE (195-290oC) Wt%													
Paraffins	13.55	10.61	13.56	16.84	14.11	11.50	15.36	19.21	19.59	16.89	13.84	15.07	16.25
Cylcoparaffins	68.56	73.28	56.71	53.13	61.43	55.96	51.14	59.31	57.92	60.92	58.20	56.39	55.05
Aromatics, total	17.89	16.10	29.73	30.03	24.46	32.54	33.50	21.48	22.49	22.16	27.90	28.53	28.68
mono-	17.41	15.75	29.06	29.56	24.12	32.00	33.13	21.25	22.26	21.39	26.39	28.13	28.21
di-	0.45	0.33	0.66	0.44	0.34	0.54	0.32	0.13	0.19	0.73	0.40	0.39	0.45
tri-	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.99	0.00	0.00
PNA	0.03	0.02	0.01	0.03	0.00	0.00	0.05	0.10	0.04	0.04	0.12	0.01	0.02
Others	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.07	0.00	0.00

TABLE 3 (cont.)

Cat. A - DENITROGENATED SYNCRUDE GAS-OIL (cont.)

Run #	1	2	3	4	5	6	7	8	9	10	11	12(NH3)	13(NH3)
DISTILLATE (290-315oC) Wt%													
Paraffins	11.10	8.52	8.33	9.66	7.12	6.75	7.42	9.16	8.85	8.37	10.04	8.17	9.82
Cylcoparaffins	63.27	70.33	55.77	55.93	60.89	54.41	45.57	62.22	54.40	52.13	49.32	58.04	50.93
Aromatics, total	25.44	20.76	35.64	36.35	31.68	38.60	46.52	28.61	36.72	39.36	40.58	33.46	39.18
mono-	21.85	17.49	33.05	33.67	28.42	34.92	41.88	26.49	34.35	36.18	37.24	30.49	36.41
di-	1.85	0.91	1.48	1.62	1.39	1.82	2.70	0.98	1.35	1.69	2.35	1.44	1.56
tri-	1.64	2.28	0.98	0.88	1.79	1.65	1.52	1.00	0.84	1.14	0.89	1.45	1.11
PNA	0.10	0.08	0.13	0.18	0.08	0.21	0.42	0.14	0.18	0.35	0.10	0.08	0.10
Others	0.19	0.39	0.28	0.05	0.31	0.25	0.48	0.01	0.03	0.14	0.07	0.33	0.09
GAS-OIL (315oC+) Wt%													
Paraffins	17.88	12.08	7.66	7.26	8.44	7.58	7.47	7.47	8.19	7.70	8.31	8.10	7.61
Cycloparaffins	67.33	71.69	59.95	54.68	61.00	57.75	54.22	58.92	58.97	54.13	53.38	62.21	56.69
mono-	22.84	18.61	15.90	15.21	13.85	14.62	13.36	14.60	15.53	14.11	13.60	15.95	13.56
di-	20.12	21.21	16.26	15.01	16.33	14.84	14.22	15.21	16.10	14.03	14.38	17.25	14.59
tri-	13.82	18.57	13.46	11.42	13.17	12.06	11.69	12.39	12.17	10.72	11.09	13.45	12.02
tetra-	10.55	13.13	9.26	8.69	10.88	9.80	9.97	9.91	9.09	8.17	9.31	10.48	9.69
penta-	0.00	0.17	3.54	3.15	6.77	4.19	4.98	4.56	4.15	4.18	5.00	3.76	4.97
hexa-	0.00	0.00	1.53	1.19	0.00	2.23	0.00	2.25	1.93	2.92	0.00	1.31	1.87
Aromatics	14.03	15.75	30.74	35.21	28.68	32.49	35.96	31.13	30.74	35.21	36.49	28.14	33.40
mono-	10.04	11.73	20.96	23.40	19.17	22.03	24.05	21.06	20.85	22.75	22.57	19.20	22.13
di-	2.95	3.18	7.40	8.64	7.20	8.17	8.90	7.70	7.46	9.48	9.84	6.60	8.48
tri-	0.53	0.50	1.74	2.36	1.45	1.67	2.19	1.62	1.91	2.29	3.15	1.69	1.95
tetra-	0.50	0.26	0.31	0.44	0.37	0.11	0.36	0.14	0.75	0.24	0.57	0.33	0.27
penta-	0.01	0.08	0.33	0.37	0.49	0.51	0.46	0.61	0.77	0.45	0.36	0.32	0.57
Others	0.76	0.48	1.66	2.85	1.88	2.18	2.35	2.49	2.09	2.97	1.82	1.57	2.29

TABLE 4

Cat. A - RAW SYNCRUDE GAS-OIL

Run #	1	2	3	4	5	6	7	8	9	10	11
REACTION CONDITIONS											
Temperature (oC)	415	395	395	395	383	383	383	370	370	370	370
LHSV	1.00	0.50	1.00	2.00	0.50	1.00	2.00	0.50	1.00	2.00	1.00
Pressure (psi)	2750	2750	2750	2750	2750	2750	2750	2750	2750	2750	1500
H2/Feed (SCFB)	5000	5000	5000	5000	5000	5000	5000	5000	5000	5000	5000
H2 consumption (SCFB)	1069	946	623	517	786	377	352	672	331	260	320
INSPECTION DATA											
total N in TLP (ppm)	5.2	15.0	186.0	634.0	73.0	458.00	458.00	259.00	678.00	1137.00	1246.00
total S in TLP (ppm)	65	67	455	1253	257	519	1588	638	1475	2190	1926
total N in 315oC+ Resid (ppm)	17	28	210	585	96	436	732	253	635	993	1104
total S in 315oC+ Resid (ppm)	120	121	506	1241	304	947	1660	628	1473	2164	1862
density @15C liquid product	0.8757	0.8916	0.9169	0.9264	0.9117	0.9246	0.9312	0.9216	0.9315	0.9352	0.9220
PRODUCT YIELD WT%											
Gas	2.50	2.70	1.30	1.10	1.50	0.60	0.60	0.70	0.70	0.60	0.60
Naphtha (IBP-195oC)	12.20	7.90	2.60	0.00	3.40	0.70	0.00	1.40	0.70	0.00	0.00
Lt Distillate (195-290oC)	18.80	10.50	3.80	2.90	4.60	2.80	1.60	1.50	0.70	0.50	1.00
Hy Distillate (290-315oC)	8.40	8.00	5.20	3.80	4.70	2.70	1.20	2.40	1.00	0.90	1.00
Gas-Oil (315oC+)	58.10	70.90	87.10	92.20	85.80	93.20	96.60	94.00	96.90	98.00	97.40
NAPHTHA (BP-195oC) Vol%											
Paraffins	38.05	32.48	33.14	-	32.45	34.34	-	30.71	36.07	-	-
Isoparaffins	32.04	22.81	22.50		23.39	23.59		20.78	24.15		
n-paraffins	6.11	9.68	10.64		9.06	10.75		9.94	11.92		
Naphtenes	51.29	57.09	54.09	-	56.47	54.44	-	57.41	53.66	-	-
Aromatics	10.56	10.42	12.77	-	11.08	11.22	-	11.82	10.27	-	-
DISTILLATE (195-290oC) Wt%											
Paraffins	12.61	10.98	13.84	19.41	11.52	13.90	17.59	11.55	12.36	14.95	17.58
Cylcoparaffins	52.31	57.07	47.07	47.97	52.37	48.73	48.11	55.01	48.50	46.80	42.91
Aromatics, total	35.08	31.94	39.13	32.62	36.11	37.06	33.99	33.40	39.14	38.19	39.46
mono-	33.92	31.34	38.51	32.33	35.44	36.94	33.65	32.46	38.11	36.70	38.44
di-	1.08	0.60	0.62	0.29	0.59	0.00	0.24	0.73	1.02	1.12	0.81
tri-	0.00	0.00	0.00	0.00	0.03	0.00	0.00	0.20	0.00	0.32	0.20
PNA	0.08	0.00	0.00	0.00	0.05	0.12	0.10	0.01	0.01	0.05	0.01
Others	0.00	0.00	0.00	0.00	0.00	0.32	0.30	0.05	0.00	0.06	0.05

TABLE 4 (cont.)

Cat. A - RAW SYNCRUDE GAS-OIL (cont.)

Run #	1	2	3	4	5	6	7	8	9	10	11
DISTILLATE (290-315oC) Wt%											
Paraffins	7.92	6.30	7.02	7.40	6.32	6.16	7.04	5.23	6.46	7.82	9.04
Cylcoparaffins	49.69	61.97	45.65	42.52	50.71	43.67	40.42	56.85	45.01	42.86	40.60
Aromatics, total	41.84	31.11	46.79	49.12	42.58	49.35	51.69	37.67	47.50	48.38	49.17
mono-	36.37	25.60	42.24	41.57	38.45	44.50	45.70	32.97	41.48	42.38	39.99
di-	3.57	2.88	3.13	6.01	2.37	3.29	4.64	2.86	4.53	4.54	7.21
tri-	1.80	2.42	1.32	1.38	1.67	1.35	1.16	1.50	1.37	1.23	1.63
PNA	0.10	0.21	0.10	0.16	0.09	0.21	0.19	0.34	0.12	0.23	0.34
Others	0.55	0.62	0.55	0.97	0.39	0.82	0.85	0.25	1.03	0.93	1.19
GAS-OIL (315oC+) Wt%											
Paraffins	11.56	8.27	7.71	7.64	7.75	6.62	6.20	7.48	5.85	6.26	6.60
Cycloparaffins	58.04	63.61	52.44	51.91	55.58	43.41	41.91	53.02	40.89	40.39	43.21
mono-	15.99	15.65	13.42	13.01	13.75	10.85	11.31	13.45	11.17	10.03	11.28
di-	15.94	16.47	13.89	14.08	14.59	11.41	11.13	13.98	10.59	10.17	11.50
tri-	13.19	14.49	10.14	11.02	11.58	8.79	8.07	10.46	8.04	7.71	8.03
tetra-	12.92	10.49	9.02	9.02	10.50	7.25	6.78	8.10	6.71	7.16	7.30
penta-	0.00	4.71	3.75	3.06	5.11	3.55	3.09	4.58	2.91	3.45	3.67
hexa-	0.00	1.80	2.22	1.72	0.05	1.56	1.53	2.45	1.47	1.87	1.43
Aromatics	28.57	26.59	37.56	37.86	34.27	44.60	46.92	36.71	47.57	48.33	45.75
mono-	18.13	17.22	23.31	21.67	22.23	7.26	28.01	23.83	28.88	27.38	24.92
di-	7.94	7.19	10.55	10.62	9.07	22.07	13.48	9.79	12.96	13.95	13.58
tri-	1.80	1.63	2.86	4.12	2.07	13.62	3.61	2.38	3.52	4.76	4.93
tetra-	0.58	0.33	0.48	0.91	0.33	1.28	0.92	0.24	1.02	1.03	1.45
penta-	0.12	0.22	0.36	0.54	0.57	0.37	0.90	0.47	1.19	1.21	0.87
Others	1.82	1.52	2.30	2.59	2.40	5.37	4.97	2.79	5.68	5.01	4.47

TABLE 5

SHELL 411 - DENITROGENATED SYNCRUDE GAS-OIL

Run #	1	2	3	4	5	6	7	8	9	10	11
REACTION CONDITIONS											
Temperature (oC)	415	395	395	395	383	383	383	370	370	370	370
LHSV	1.00	0.50	1.00	2.00	0.50	1.00	2.00	0.50	1.00	2.00	1.00
Pressure (psi)	2750	2750	2750	2750	2750	2750	2750	2750	2750	2750	1500
H2/Feed (SCFB)	5000	5000	5000	5000	5000	5000	5000	5000	5000	5000	5000
H2 consumption (SCFB)	646	601	361	193	486	314	129	234	111	12	69
INSPECTION DATA											
total N in TLP (ppm)	1.4	1.0	2.9	19.0	5.3	17.0	79.0	17.5	77.0	107.0	123.0
total S in TLP (ppm)	7	8	5	9	14	22	65	20	202	125	77
total N in 315oC+ Resid (ppm)	1.4	0.6	10.9	80.0	2.3	31.9	183.0	217.0	54.0	103.0	121.0
total S in 315oC+ Resid (ppm)	70	84	62	82	69	89	111	60	105	154	115
density @15C liquid product	0.8587	0.8756	0.8862	0.9061	0.8934	0.9062	0.9140	0.9053	0.9133	0.9176	0.9171
PRODUCT YIELD WT%											
Gas	1.8	1.4	1.3	0.6	0.7	0.7	0.6	0.6	0.2	0.3	0.3
Naphtha (IBP-195oC)	14.3	6.9	4.1	2.2	2.8	1.7	1.6	0.9	0.0	0.0	0.6
Lt Distillate (195-290oC)	19.6	11.4	7.0	3.1	5.4	1.8	0.9	2.0	1.5	0.8	1.7
Hy Distillate (290-315oC)	9.5	8.3	3.3	2.4	5.2	3.6	1.8	3.5	1.8	1.0	1.8
Gas-Oil (315oC+)	54.8	72.0	84.3	91.7	85.9	92.2	95.1	93.0	96.5	97.9	95.6
NAPHTHA (BP-195oC) Vol%											
Paraffins	36.01	37.40	35.05	31.46	36.97	30.16	30.81	27.21	-	-	29.45
Isoparaffins	0.00	12.07	24.72	20.09	28.33	19.51	19.23	17.43			25.18
n-paraffins	36.01	25.34	1033.00	11.37	8.64	10.66	11.58	9.78			4.27
Naphtenes	55.95	57.59	57.61	56.27	58.89	59.89	56.18	64.53	-	-	58.57
Aromatics	8.04	5.01	7.34	12.28	4.14	9.94	13.00	8.27	-	-	11.98
DISTILLATE (195-290oC) Wt%											
Paraffins	12.94	10.90	10.78	11.43	10.62	10.72	11.62	10.99	14.58	10.56	11.41
Cylcoparaffins	73.77	80.16	68.31	55.23	77.33	63.14	53.01	70.00	61.55	56.65	54.91
Aromatics, total	13.29	8.94	20.83	33.30	12.04	26.14	35.12	19.00	23.85	32.48	33.68
mono-	12.92	8.19	19.83	32.21	11.33	25.38	34.21	18.44	23.32	31.63	32.40
di-	0.37	0.11	0.29	0.48	0.09	0.33	0.19	0.09	0.01	0.06	0.68
tri-	0.00	0.60	0.69	0.46	0.62	0.43	0.55	0.45	0.41	0.62	0.42
PNA	0.00	0.04	0.02	0.15	0.00	0.00	0.17	0.02	0.11	0.17	0.18
Others	0.00	0.00	0.07	0.03	0.00	0.00	0.25	0.00	0.02	0.30	0.01

TABLE 5 (cont.)

SHELL 411 - DENITROGENATED SYNCRUDE GAS-OIL (cont.)

Run #	1	2	3	4	5	6	7	8	9	10	11
DISTILLATE (290-315oC) Wt%											
Paraffins	6.51	6.77	6.60	6.68	3.49	6.44	12.09	4.75	6.16	6.65	7.57
Cycloparaffins	75.68	78.36	67.63	55.91	80.36	64.17	45.12	69.95	59.25	53.79	49.10
Aromatics, total	17.10	13.88	24.58	36.85	15.39	28.75	42.40	24.35	34.00	38.21	42.99
mono-	12.74	9.25	19.94	32.56	11.29	24.00	38.61	20.19	29.17	34.63	37.74
di-	1.60	0.59	1.11	1.88	0.62	1.75	1.70	0.63	1.87	1.20	3.20
tri-	2.69	3.81	3.26	2.05	3.24	2.68	1.70	3.06	2.48	2.01	1.86
PNA	0.07	0.23	0.27	0.36	0.24	0.32	0.39	0.47	0.48	0.37	0.19
Others	0.70	0.98	1.19	0.55	0.75	0.64	0.39	0.95	0.58	1.35	0.34
GAS-OIL (315oC+) Wt%											
Paraffins	12.73	10.17	8.06	7.46	7.62	6.38	6.37	5.64	6.31	6.02	7.75
Cycloparaffins	66.19	77.73	68.87	62.84	79.68	64.84	58.79	69.19	56.04	54.79	56.71
mono-	20.83	19.94	17.22	16.44	19.87	17.03	15.60	18.10	14.12	15.13	15.01
di-	20.08	31.81	18.31	16.68	20.96	17.59	16.13	18.42	14.91	14.66	16.03
tri-	14.58	18.21	15.16	12.76	18.21	13.68	11.99	15.09	12.23	11.00	10.71
tetra-	10.70	12.29	10.67	9.69	12.71	10.09	9.24	11.56	8.93	8.56	8.46
penta-	0.00	5.47	5.06	4.73	5.47	4.49	3.85	4.37	4.08	3.52	4.28
hexa-	0.00	0.01	2.47	2.54	2.47	1.96	1.98	1.66	1.72	1.93	2.20
Aromatics	19.72	10.92	21.58	28.01	11.50	27.07	32.82	22.99	34.50	36.17	33.57
mono-	13.38	6.84	18.35	18.52	7.44	18.21	21.80	14.99	22.55	24.32	20.87
di-	4.70	2.95	5.76	7.04	2.98	6.64	8.22	5.32	8.40	8.58	8.06
tri-	0.89	0.52	1.26	1.68	0.72	1.51	2.01	0.97	1.52	1.83	2.69
tetra-	0.60	0.35	0.25	0.29	0.09	0.18	0.20	0.69	0.76	0.37	0.65
penta-	0.15	0.26	0.46	0.48	0.27	0.53	0.59	1.02	1.27	1.07	0.50
Others	1.37	1.18	1.50	1.70	1.19	1.71	2.03	2.17	3.14	3.02	1.99

TABLE 6

SHELL 411- RAW SYNCRUDE GAS-OIL

Run #	1	2	3	4	5	6	7	8	9	10	11
REACTION CONDITIONS											
Temperature (oC)	415	395	395	395	383	383	383	370	370	370	370
LHSV	1.00	0.50	1.00	2.00	0.50	1.00	2.00	0.50	1.00	2.00	1.00
Pressure (psi)	2750	2750	2750	2750	2750	2750	2750	2750	2750	2750	1500
H2/Feed (SCFB)	5000	5000	5000	5000	5000	5000	5000	5000	5000	5000	5000
H2 consumption (SCFB)	1238	1336	1099	819	1048	755	578	902	702	445	480
INSPECTION DATA											
total N in TLP (ppm)	11.0	0.9	11.6	70.0	7.8	83.0	164.0	25.0	126.0	333.0	444.0
total S in TLP (ppm)	106	30	70	200	70	100	240	60	190	490	350
total N in 315oC+ Resid (ppm)	4	3	5	160	6	127	490	22	83	292	433
total S in 315oC+ Resid (ppm)	105	27	90	133	103	199	248	117	217	502	342
density @15C liquid product	0.8636	0.8618	0.8810	0.9030	0.8897	0.9046	0.9157	0.9038	0.9150	0.9230	0.9220
PRODUCT YIELD WT%											
Gas	4.10	3.50	1.50	2.20	1.00	1.10	0.60	0.80	3.20	1.10	0.90
Naphtha (IBP-195oC)	13.30	9.90	7.30	3.60	4.40	2.80	2.20	2.30	1.40	0.00	0.90
Lt Distillate (195-290oC)	17.40	14.60	9.90	4.90	6.50	3.60	2.00	3.20	1.90	1.40	2.00
Hy Distillate (290-315oC)	10.10	10.00	7.20	4.10	4.80	4.20	3.00	3.30	1.80	0.90	3.00
Gas-Oil (315oC+)	55.10	62.00	74.10	85.20	83.30	88.30	92.70	90.40	91.70	96.60	93.20
NAPHTHA (BP-195oC) Vol%											
Paraffins	37.53	36.79	34.17	33.91	33.17	32.89	28.99	25.73	25.82	-	26.67
Isoparaffins	26.70	29.64	28.85	24.56	22.79	25.38	18.14	17.46	19.33		16.61
n-paraffins	10.65	7.14	5.86	9.35	10.38	7.51	10.85	8.27	6.49		10.06
Naphtenes	57.07	61.92	60.47	56.52	63.30	58.33	60.02	57.91	64.44	-	59.76
Aromatics	5.59	1.30	4.82	9.57	3.53	8.78	10.98	16.31	9.73	-	15.37
DISTILLATE (195-290oC) Wt%											
Paraffins	11.34	10.50	8.05	8.21	9.09	9.67	9.51	8.09	7.96	9.79	10.00
Cylcoparaffins	75.03	85.64	79.35	66.56	82.79	65.98	59.61	75.02	63.27	62.07	53.25
Aromatics, total	13.63	3.86	12.56	25.08	8.12	24.07	30.87	16.73	28.70	28.14	36.75
mono-	13.32	3.22	12.12	24.13	7.67	24.03	30.24	16.19	27.78	28.11	35.87
di-	0.26	0.06	0.31	0.85	0.01	0.03	0.56	0.00	0.27	0.00	0.87
tri-	0.00	0.58	0.13	0.00	0.44	0.00	0.00	0.53	0.55	0.00	0.00
PNA	0.05	0.00	0.00	0.10	0.00	0.01	0.07	0.01	0.10	0.03	0.01
Others	0.00	0.00	0.00	0.14	0.00	0.00	0.00	0.00	0.06	0.00	0.00

TABLE 6 (cont.)

SHELL 411 - RAW SYNCRUDE GAS-OIL (cont.)

Run #	1	2	3	4	5	6	7	8	9	10	11
DISTILLATE (290-315oC) Wt%											
Paraffins	6.81	5.28	3.57	3.79	4.57	3.59	3.30	3.24	3.58	4.42	5.26
Cylcoparaffins	71.13	83.17	78.29	61.35	81.14	65.18	56.47	75.49	62.00	55.89	47.13
Aromatics, total	21.16	10.58	17.83	34.30	13.64	30.92	40.00	20.73	34.20	41.43	47.01
mono-	17.23	5.45	15.12	30.50	10.24	27.70	36.03	17.48	30.67	37.85	39.43
di-	1.05	0.56	0.53	1.86	0.22	1.29	2.31	0.36	1.58	2.23	5.51
tri-	2.58	4.50	2.15	1.78	3.12	1.79	1.46	2.74	1.81	1.08	1.71
PNA	0.30	0.07	0.03	0.16	0.06	0.14	0.20	0.15	0.14	0.27	0.36
Others	0.90	0.96	0.32	0.56	0.65	0.31	0.24	0.54	0.21	0.26	0.61
GAS-OIL (315oC+) Wt%											
Paraffins	10.18	11.51	10.33	9.20	10.25	7.74	7.01	8.93	7.51	6.32	6.36
Cycloparaffins	65.93	80.28	69.71	56.34	73.92	59.30	51.67	70.02	53.77	45.67	48.55
mono-	19.16	23.11	17.96	13.67	15.52	14.12	12.80	14.45	11.69	11.18	12.68
di-	18.28	24.35	19.22	15.93	19.82	15.68	13.35	18.01	14.09	11.77	12.61
tri-	14.81	18.06	17.95	13.31	19.62	14.76	11.63	18.09	14.03	10.13	9.65
tetra-	10.12	10.03	14.58	13.43	18.97	14.73	9.22	19.48	13.96	8.05	7.48
penta-	3.56	4.74	0.00	0.00	0.00	0.00	4.67	0.00	0.00	4.53	3.70
hexa-	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.43
Aromatics	22.14	7.54	18.46	32.35	14.52	30.46	37.98	19.20	35.37	44.64	42.71
mono-	14.95	4.52	12.30	20.78	9.46	19.92	23.67	12.42	22.87	29.03	25.91
di-	5.51	2.16	4.34	8.26	3.77	7.34	10.26	4.67	8.57	11.87	12.32
tri-	0.93	0.51	0.93	1.83	0.60	1.43	2.44	0.84	1.57	2.55	3.52
tetra-	0.42	0.21	0.60	0.78	0.28	0.82	0.67	0.55	0.92	0.26	0.40
penta-	0.33	0.14	0.39	0.70	0.41	0.95	0.94	0.72	1.44	0.93	0.56
Others	1.55	0.68	1.49	2.11	1.31	2.50	3.35	1.86	3.35	3.37	2.38

TABLE 7

SHELL 753 - DENITROGENATED SYNCRUDE GAS-OIL

Run #	1	2	3	4	5	6	7	8	9	10	11
REACTION CONDITIONS											
Temperature (oC)		395	395	395	383	383	383	370		370	370
LHSV		0.50	1.00	2.00	0.50	1.00	2.00	0.50		2.00	1.00
Pressure (psi)		2750	2750	2750	2750	2750	2750	2750		2750	1500
H2/Feed (SCFB)		5000	5000	5000	5000	5000	5000	5000		5000	5000
H2 consumption (SCFB)		2329	1531	466		945	179	1589		165	245
INSPECTION DATA											
total N in TLP (ppm)		0.3	2.9	19.0	-	14.0	47.0	< .1		73.0	46.0
total S in TLP (ppm)		3	5	9	-	9	118	3		187	167
density @15C liquid product		0.7178	0.7316	0.8505	0.7235	0.7952	0.8874	0.7568		0.8954	0.8873
PRODUCT YIELD WT%											
Gas		-	6.6	1.9	-	2.8	0.9	4.2		0.7	0.8
Naphtha (IBP-195oC)		91.5	84.3	26.7	95.0	52.2	11.0	76.4		9.9	12.8
Lt Distillate (195-290oC)		8.5	9.1	15.9	4.1	21.1	9.9	15.2		7.2	8.8
Hy Distillate (290-315oC)		0.0	0.0	2.9	0.0	2.1	2.3	1.4		3.1	3.0
Gas-Oil (315oC+)		0.0	0.0	52.6	0.0	21.8	75.9	2.8		79.1	74.6
NAPHTHA (IBP-195oC) Vol%											
Paraffins				35.51		39.07		21.60		18.80	21.56
Isoparaffins				35.51		39.07		19.10		17.18	17.32
n-paraffins				0.00		0.00		2.50		1.62	4.25
Naphtenes				52.86		52.13		61.66		64.85	63.54
Aromatics				11.63		8.80		16.74		16.34	14.90
DISTILLATE (195-290oC) Wt%											
Paraffins				11.57		18.18		7.35		5.84	7.85
Cycloparaffins				42.84		48.72		41.38		41.55	44.82
Aromatics, total				45.59		33.10		50.87		52.56	47.32
mono-				43.47		32.09		48.89		50.88	45.86
di-				2.12		1.01		1.91		1.62	1.28
tri-				0.00		0.00		0.00		0.00	0.11
PNA				0.00		0.00		0.07		0.06	0.07
Others				0.00		0.00		0.00		0.05	0.00

TABLE 7 (cont.)

SHELL 753 - DENITROGENATED SYNCRUDE GAS-OIL (cont.)

Run #	1	2	3	4	5	6	7	8	9	10	11
DISTILLATE (290-315oC) Wt%											
Paraffins				11.07		22.13		6.97		5.56	7.47
Cycloparaffins				40.55		45.74		40.17		41.06	44.27
Aromatics, total				48.16		32.05		52.68		53.29	48.19
mono-				38.82		23.92		44.68		46.94	43.64
di-				8.11		7.24		6.11		4.64	2.96
tri-				1.03		0.72		1.66		1.50	1.49
PNA				0.20		0.17		0.23		0.21	0.10
Others				0.22		0.07		0.19		0.09	0.09
GAS-OIL (315oC+) Wt%											
Paraffins				12.90		22.44		10.57		9.55	9.11
Cycloparaffins				60.91		62.66		57.66		58.75	61.11
mono-				16.42		19.86		15.04		14.32	18.64
di-				15.64		17.44		15.82		15.04	15.82
tri-				12.32		10.98		13.97		12.63	11.51
tetra-				10.45		8.50		8.48		9.79	9.31
penta-				6.09		5.83		4.35		6.97	4.60
hexa-				0.00		0.06		0.00		0.00	3.03
Aromatics				24.72		13.95		29.93		29.91	28.02
mono-				14.81		7.63		17.37		18.63	18.48
di-				7.03		4.37		9.12		8.22	7.26
tri-				1.66		1.14		2.45		1.97	1.44
tetra-				0.72		0.55		0.39		0.39	0.11
penta-				5.00		0.26		0.60		0.70	0.73
Others				1.48		0.96		1.84		1.79	1.76

TABLE 8

SHELL 753- RAW SYNCRUDE GAS-OIL

Run #	1	2	3	4	5	6	7	8	9	10	11
REACTION CONDITIONS											
Temperature (oC)		395	395	395	383	383	383	370	370	370	370
LHSV		0.50	1.00	2.00	0.50	1.00	2.00	0.50	1.00	2.00	1.00
Pressure (psi)		2750	2750	2750	2750	2750	2750	2750	2750	2750	1500
H2/Feed (SCFB)		5000	5000	5000	5000	5000	5000	5000	5000	5000	5000
H2 consumption (SCFB)		2008	1197	782	1371	1033	699	1177	738	649	810
INSPECTION DATA											
total N in TLP (ppm)		1.6	2.8	40.0	1.4	9.6	106.0	4.3	34.2	213.0	34.9
total S in TLP (ppm)		90	100	127	102	100	174	82	100	271	150
density @15C liquid product		0.7787	0.8536	0.9044	0.8357	0.8746	0.9069	n/a	0.8976	0.9203	0.8757
PRODUCT YIELD WT%											
Gas		3.50	1.20	1.20	1.90	1.20	0.50	1.30	0.70	0.30	1.70
Naphtha (IBP-195oC)		57.40	20.50	5.50	29.30	14.00	4.70	16.20	5.90	0.60	18.40
Lt Distillate (195-290oC)		23.90	17.70	5.30	23.60	13.30	5.50	18.10	7.30	0.90	15.50
Hy Distillate (290-315oC)		2.80	4.40	4.00	4.90	3.80	2.80	4.10	3.70	1.40	5.60
Gas-Oil (315oC+)		12.40	56.20	84.00	40.30	67.70	86.50	60.30	82.40	96.80	58.80
NAPHTHA (IBP-195oC) Vol%											
Paraffins		36.07	31.31	20.46	31.18	47.22	18.11	27.97	23.63	18.67	25.28
Isoparaffins		34.26	30.29	18.73	31.07	24.75	18.11	27.42	21.20	13.13	23.25
n-paraffins		1.80	1.03	1.72	0.11	22.46	0.00	0.55	2.43	5.54	2.03
Naphtenes		60.50	60.20	64.04	60.86	43.82	65.81	63.77	62.84	67.85	60.59
Aromatics		3.44	8.49	15.51	7.97	8.96	16.08	8.26	13.52	13.47	14.13
DISTILLATE (195-290oC) Wt%											
Paraffins		21.65	9.98	7.71	12.44	5.32	6.11	6.76	5.57	7.51	8.10
Cycloparaffins		66.41	67.67	64.96	71.98	56.30	55.37	75.79	52.45	51.92	39.39
Aromatics, total		11.95	22.35	27.33	15.58	38.38	38.52	17.45	41.98	40.57	52.51
mono-		9.97	21.87	26.73	14.47	37.69	37.61	17.10	41.44	39.48	49.59
di-		1.98	0.48	0.56	1.09	0.65	0.86	0.35	0.54	1.08	2.92
tri-		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PNA		0.00	0.00	0.04	0.02	0.04	0.05	0.00	0.00	0.01	0.00
Others		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

TABLE 8 (cont.)

SHELL 753 - RAW SYNCRUDE GAS-OIL (cont.)

Run #	1	2	3	4	5	6	7	8	9	10	11
DISTILLATE (290-315oC) Wt%											
Paraffins		27.31	9.97	7.97	13.05	4.65	5.85	9.13	5.38	7.49	9.15
Cycloparaffins		56.84	61.68	57.84	70.55	50.55	50.10	67.33	48.04	58.27	34.65
Aromatics, total		15.83	28.27	34.08	16.27	44.80	44.05	23.13	46.50	34.22	55.94
mono-		11.15	25.33	30.21	13.48	42.38	40.47	19.51	42.03	31.93	44.92
di-		4.29	1.60	2.11	1.50	1.66	2.46	1.33	2.12	2.07	9.71
tri-		0.38	1.29	1.63	1.29	0.73	1.07	2.28	2.11	0.11	1.31
PNA		0.01	0.05	0.13	0.00	0.03	0.05	0.01	0.24	0.11	0.00
Others		0.01	0.00	0.10	0.14	0.00	0.00	0.41	0.09	0.01	0.09
GAS-OIL (315oC+) Wt%											
Paraffins		32.00	13.46	8.62	16.36	10.39	8.17	12.36	8.82	7.82	11.95
Cycloparaffins		60.17	63.06	59.13	69.97	65.04	57.45	69.83	60.47	56.37	59.51
mono-		27.56	18.75	14.96	22.28	17.86	15.11	19.27	14.40	14.50	16.30
di-		16.58	18.33	15.25	18.74	17.31	14.87	17.83	15.63	15.05	15.28
tri-		8.41	15.97	12.65	14.20	13.79	12.28	15.53	13.19	11.45	12.63
tetra-		7.61	10.02	10.49	9.99	10.19	8.79	12.45	9.87	8.90	8.93
penta-		0.00	0.00	5.77	4.77	5.11	4.60	4.76	5.79	3.75	5.32
hexa-		0.00	0.00	0.00	0.00	0.78	1.80	0.00	1.59	2.72	1.05
Aromatics		6.74	22.34	30.19	12.72	23.09	32.30	16.48	28.42	33.59	27.05
mono-		5.09	17.34	19.75	8.90	15.63	21.04	11.28	18.57	22.22	14.09
di-		1.27	3.69	7.81	2.61	5.60	8.50	3.98	7.24	8.53	8.59
tri-		0.16	0.84	1.80	0.69	1.23	1.89	0.68	1.55	2.19	2.66
tetra-		0.15	0.20	0.31	0.26	0.18	0.31	0.14	0.30	0.31	1.17
penta-		0.07	0.27	0.52	0.26	0.45	0.56	0.40	0.76	0.34	0.54
Others		1.10	1.13	2.06	0.95	1.50	2.07	1.32	2.29	2.23	1.48

TABLE 9A

DENITROGENATED SYNCRUDE GAS-OIL - HIGH SEVERITY TESTS

Run #	9	4	3	8	5	2	7	6	1
REACTION CONDITIONS									
Temperature (oC)	415	415	415	408	408	408	400	400	400
LHSV	0.25	0.50	1.00	0.25	0.50	1.00	0.25	0.50	1.00
Pressure (psi)	2750	2750	2750	2750	2750	2750	2750	2750	2750
H2/Feed (SCFB)	5000	5000	5000	5000	5000	5000	5000	5000	5000
total N in Feed (ppm)	394	394	394	394	394	394	394	394	394
INSPECTION DATA									
total N (ppm)	0.4	0.2	0.6	0.2	0.7	0.4	0.0	0.5	0.5
total S (ppm)	16	94	69	0	10	68	0	11	71
density @15C liquid product	0.7747	0.7762	0.7867	0.7737	0.8050	0.8037	0.7957	0.8363	0.8335
gas	0.4400	0.4400	0.4400	0.4400	0.4400	0.4400	0.4400	0.4400	0.4400
naphtha	0.7461	0.7474	0.7501	0.7459	0.7635	0.7563	0.7530	0.7642	0.7609
distillate	0.8228	0.8252	0.8303	0.8214	0.8380	0.8380	0.8321	0.8509	0.8496
gas-oil	0.8400	0.8566	0.8528	0.8487	0.8636	0.8590	0.8525	0.8770	0.8727
RAW DATA									
gas yield (g/D)	4.40	4.90	8.20	2.90	3.60	6.50	1.60	3.80	4.40
liquid yield (g/D)	70.70	157.10	94.10	69.80	163.40	306.00	74.80	162.70	314.80
Naphtha %wt	71.15	62.92	52.67	61.39	45.07	41.30	46.09	25.62	27.57
Distillate %wt	26.23	31.89	37.83	33.13	42.81	37.28	34.16	34.40	31.44
Gas-Oil %wt	2.62	5.18	9.49	5.48	12.13	21.42	15.80	39.98	40.99
PRODUCT YIELD WT%									
Gas	5.86	3.02	8.02	3.99	2.16	2.08	2.09	2.28	1.38
Naphtha (IBP-195oC)	66.98	61.02	48.45	58.94	44.10	40.44	45.12	25.04	27.19
Distillate (195oC-315oC)	24.69	30.93	34.80	31.81	41.89	36.50	33.44	33.61	31.01
Gas-Oil (315oC+)	2.47	5.02	8.73	5.26	11.87	20.97	15.47	39.07	40.42
PRODUCT COMPOSITION VOL%									
Gas	9.79	5.21	13.50	6.82	3.88	3.75	3.87	4.25	2.57
Naphtha (IBP-195oC)	65.99	61.92	47.86	59.41	45.70	42.38	48.71	26.85	29.37
Distillate (195oC-315oC)	22.06	28.42	31.06	29.11	39.55	34.52	32.67	32.38	29.99
Gas-Oil (315oC+)	2.16	4.45	7.58	4.66	10.87	19.35	14.75	36.51	38.07
PRODUCT YIELD Vol / Vol of Feed *100									
Naphtha (IBP - 195oC)	83.16	75.62	59.83	73.20	53.50	49.53	55.51	30.35	33.10
Distillate (195-315 oC)	27.80	34.71	38.82	35.87	46.30	40.35	37.23	36.59	33.81
Gas-Oil (3150C +)	2.72	5.43	9.48	5.74	12.73	22.62	16.81	41.26	42.91
Total Liquid Yield	113.68	115.77	108.13	114.81	112.53	112.50	109.55	108.20	109.81

TABLE 9A (cont.)

DENITROGENATED SYNCRUDE GAS-OIL - HIGH SEVERITY TESTS (cont.)

Run #	9	4	3	8	5	2	7	6	1
NAPHTHA (IBP-195oC) Vol%									
Paraffins	43.97	44.20	43.45	43.53	38.17	39.35	39.24	35.90	36.19
Isoparaffins	32.00	32.34	31.26	28.61	26.55	26.73	25.28	25.87	27.27
n-paraffins	11.96	11.86	12.18	14.90	11.62	12.62	13.97	10.05	8.91
Naphtenes	53.83	52.88	52.12	54.95	55.15	56.08	59.18	58.99	58.99
Aromatics	2.21	2.92	4.43	1.52	6.68	4.58	1.58	5.11	4.82
NAPHTHA (C6-195oC) Vol%									
Paraffins	36.60	37.72	36.84	36.30	34.78	33.68	33.14	30.92	30.63
Iso-	29.90	30.07	28.81	25.78	25.18	24.30	22.69	24.20	29.65
N-	6.70	7.65	8.03	10.52	9.60	9.38	10.45	6.72	5.34
Naphtenes	60.91	59.03	58.21	61.98	58.17	61.31	65.12	63.57	64.13
Aromatics	2.50	3.26	4.95	1.71	7.05	5.00	1.74	5.51	5.24
N + 2A	65.91	65.55	68.11	65.40	72.27	71.31	68.60	74.59	74.61
DISTILLATE (195-315oC) Vol%									
Paraffins	26.84	27.98	30.68	26.47	24.65	19.55	19.41	12.95	13.50
Cylcoparaffins	64.43	60.62	54.17	67.93	56.65	66.48	74.97	68.01	71.11
Monoaromatics	8.03	10.70	14.07	5.06	17.89	13.18	4.95	18.09	14.36
Diaromatics	0.29	0.46	0.86	0.11	0.51	0.39	0.19	0.34	0.35
Triaromatics	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01
Tetraaromatics	0.00	0.03	0.00	0.00	0.02	0.02	0.00	0.03	0.03
Pentaaromatics	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Aromatics Total	8.32	11.19	14.93	5.17	18.42	13.59	5.14	18.46	14.75
Emission precursors (tri-A+)	0.00	0.03	0.00	0.00	0.02	0.02	0.00	0.03	0.04
GAS-OIL (315oC+) Wt%									
Paraffins	42.63	39.74	38.90	45.24	29.08	29.58	32.72	16.53	17.90
Cycloparaffins	37.65	45.00	50.68	45.04	57.36	61.81	61.50	68.57	70.30
mono-	20.65	24.34	28.84	26.93	26.14	31.03	33.36	24.05	26.55
Polycycloparaffins	17.00	20.66	21.84	18.11	31.22	30.78	28.14	44.52	43.75
di-	8.29	12.16	13.16	9.96	14.44	17.93	16.08	21.32	22.19
tri-	4.71	6.16	5.52	4.61	8.87	7.92	7.33	12.85	12.48
tetra-	3.11	2.35	2.32	2.70	5.78	3.88	3.98	7.34	6.71
penta-	0.97	0.00	0.84	0.83	2.13	1.05	0.76	3.01	2.37
hexa-	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Aromatics									
mono-	7.51	8.36	6.52	4.03	8.01	4.32	3.02	9.92	8.30
Polynuclear Aromatics	9.37	5.77	2.58	4.09	4.20	3.17	1.76	3.83	2.63
di-	4.60	3.26	1.56	2.05	2.87	1.54	0.98	2.64	1.86
tri-	1.59	1.01	0.41	0.67	0.64	0.55	0.30	0.54	0.29
tetra-	3.18	1.50	0.61	1.36	0.69	1.08	0.47	0.62	0.46
penta-	0.00	0.00	0.00	0.01	0.00	0.00	0.01	0.03	0.02
sulfur	1.05	0.64	0.41	0.51	0.44	0.42	0.30	0.55	0.27
Others	1.80	0.80	0.90	1.10	0.90	0.70	0.70	0.60	0.60
Gasoline Precursors	87.79	93.10	96.10	94.31	94.45	95.71	97.24	95.02	96.50

TABLE 98

RAW SYNCRUDE GAS-OIL - HIGH SEVERITY TESTS

Run #	10	15	16	11	14	17	12	13	18
REACTION CONDITIONS									
Temperature (oC)	415	415	415	408	408	408	400	400	400
LHSV	0.25	0.50	1.00	0.25	0.50	1.00	0.25	0.50	1.00
Pressure (psi)	2750	2750	2750	2750	2750	2750	2750	2750	2750
H2/Feed	5000	5000	5000	5000	5000	5000	5000	5000	5000
total N in Feed (ppm)	1665	1665	1665	1665	1665	1665	1665	1665	1665
INSPECTION DATA									
total N (ppm)	1.15	2.90	45.00	1.05	29.00	156.00	5.20	100.00	393.00
total S (ppm)	45.00	26.00	200.00	31.00	142.00	829.00	69.00	414.00	1043.00
density @15C liquid product	0.8215	0.8441	0.8800	0.8384	0.8769	0.8976	0.8585	0.8964	0.9116
gas	0.4000	0.4000	0.4000	0.4000	0.4000	0.4000	0.4000	0.4000	0.4000
naphtha	0.7527	0.7647	0.7576	0.7550	0.7584	0.7648	0.7609	0.7622	0.7665
distillate	0.8612	0.8657	0.8749	0.8647	0.8715	0.8815	0.8662	0.8760	0.8795
gas-oil	0.9024	0.9058	0.9175	0.9040	0.9185	0.9238	0.9062	0.9229	0.9298
RAW DATA									
gas yield (g/D)	3.60	5.10	5.20	3.10	3.30	4.50	2.00	1.60	2.70
liquid yield (g/D)	73.80	159.10	265.10	78.50	159.40	329.30	77.20	169.30	325.90
Naphtha %wt	37.98	23.53	14.14	29.37	15.11	7.81	20.69	8.92	3.58
Distillate %wt	43.35	41.67	30.92	39.76	25.95	22.21	30.97	17.20	11.05
Gas-Oil %wt	18.67	34.81	54.94	30.86	58.94	69.91	48.34	73.87	85.37
PRODUCT YIELD WT%									
Gas	4.65	3.11	1.92	3.80	2.03	1.35	2.53	0.94	0.82
Naphtha (IBP-195oC)	36.21	22.80	13.87	28.25	14.80	7.70	20.17	8.84	3.55
Distillate (195oC-315oC)	41.33	40.38	30.33	38.25	25.42	21.91	30.19	17.04	10.96
Gas-Oil (315oC+)	17.80	33.73	53.88	29.69	57.74	68.97	47.12	73.18	84.67
PRODUCT YIELD VOL%									
Gas	9.12	6.39	4.13	7.66	4.35	2.98	5.28	2.08	1.86
Naphtha (IBP-195oC)	37.75	24.55	15.71	30.18	16.74	8.92	22.15	10.29	4.20
Distillate (195oC-315oC)	37.65	38.40	29.75	35.67	25.01	22.00	29.12	17.26	11.31
Gas-Oil (315oC+)	15.48	30.66	50.41	26.49	53.90	66.09	43.45	70.37	82.63
PRODUCT YIELD Vol / Vol of Feed									
Naphtha (IBP - 195oC)	44.57	27.62	16.96	34.66	18.08	9.33	24.55	10.74	4.29
Distillate (195-315 oC)	44.46	43.20	32.11	40.97	27.02	23.02	32.28	18.02	11.54
Gas-Oil (3150C +)	18.27	34.49	54.40	30.42	58.23	69.15	48.16	73.45	84.35
Total Liquid Yield	107.30	105.31	103.46	106.06	103.34	101.51	105.00	102.20	100.18

TABLE 9B (cont.)

RAW SYNCRUDE GAS-OIL - HIGH SEVERITY TESTS (cont.)

Run #	10	15	16	11	14	17	12	13	18
NAPHTHA (IBP-195oC) Vol%									
Paraffins	42.76	38.17	43.62	42.69	43.14	43.16	40.13	43.42	44.62
Isoparaffins	25.39	24.29	28.18	25.59	25.74	26.85	24.20	26.90	29.89
n-paraffins	17.37	13.87	15.41	15.10	17.38	16.31	15.93	16.52	14.72
Naphtenes	49.96	52.42	45.83	49.54	46.65	45.60	51.32	46.39	45.54
Aromatics	7.28	9.41	10.55	7.76	10.21	11.24	8.55	10.19	9.84
NAPHTHA (C6-195oC) Vol%									
Paraffins	36.16	34.71	37.19	36.37	37.88	38.60	35.01	38.88	42.32
Iso-	24.11	23.54	27.46	26.65	24.96	26.41	23.21	26.41	29.80
N-	12.04	11.16	9.72	9.71	12.91	12.18	29.97	12.47	12.15
Naphtenes	55.72	55.35	51.06	55.01	50.97	49.25	55.71	50.11	47.42
Aromatics	8.12	9.94	11.75	8.62	11.15	12.14	9.28	11.01	10.25
N + 2A	71.96	75.23	74.56	72.25	73.27	73.53	74.27	72.13	67.92
DISTILLATE (195-315oC) Vol%									
Paraffins	14.18	12.99	13.13	13.66	13.75	11.66	13.30	13.30	12.77
Cylcoparaffins	56.68	55.78	48.33	55.73	48.49	45.89	57.97	45.85	44.75
Monoaromatics	27.27	29.09	34.70	28.75	35.27	39.27	26.67	38.13	39.47
Diaromatics	1.23	1.39	2.66	1.15	1.82	2.22	1.37	1.95	2.12
Triaromatics	0.00	0.00	0.48	0.00	0.00	0.03	0.00	0.03	0.15
Tetraaromatics	0.00	0.01	0.02	0.01	0.01	0.01	0.00	0.02	0.05
Pentaaromatics	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Aromatics Total	28.50	30.49	37.86	29.91	37.10	41.53	28.04	40.13	41.79
Emission precursors (tri-A+)	0.00	0.01	0.50	0.01	0.01	0.04	0.00	0.05	0.20
GAS-OIL (315oC+) Wt%									
Paraffins	13.57	7.91	5.48	12.03	8.97	5.01	10.19	8.09	4.36
Cycloparaffins	55.25	62.09	52.69	57.07	51.68	49.96	58.80	49.47	47.98
mono-	17.11	11.17	9.19	15.40	13.96	8.10	15.10	12.69	7.71
Polycycloparaffins	38.14	50.92	43.50	41.67	37.72	41.86	43.70	36.78	40.27
di-	15.73	16.54	13.17	16.15	13.59	11.86	15.92	12.67	11.77
tri-	11.09	15.01	13.40	12.07	11.27	11.77	13.04	10.67	11.10
tetra-	8.00	12.92	10.60	9.15	8.87	10.37	10.12	9.05	10.31
penta-	3.32	6.46	4.97	4.32	4.00	4.98	4.62	4.39	4.84
hexa-	0.00	0.00	1.37	0.00	0.00	2.38	0.00	0.00	2.25
Aromatics									
mono-	18.10	15.37	20.61	18.69	22.45	20.87	19.08	23.76	22.41
Polynuclear Aromatics	11.14	12.42	18.91	10.36	14.67	21.35	10.04	15.86	21.62
di-	7.86	8.84	13.30	7.79	10.97	14.55	7.76	11.61	14.44
tri-	1.85	2.05	4.03	1.54	2.73	4.50	1.56	3.02	5.04
tetra-	1.40	1.44	1.14	0.98	0.78	1.75	0.64	0.85	1.42
penta-	0.03	0.09	0.44	0.05	0.19	0.55	0.08	0.38	0.72
sulfur	1.05	1.31	1.61	1.04	1.54	2.43	1.19	2.02	2.08
Others	0.90	0.90	0.70	0.80	0.70	0.88	0.70	0.81	1.56
Gasoline Precursors	86.92	85.37	78.78	87.79	83.10	75.84	88.07	81.32	74.75

TABLE 10

EFFECT OF FEED PRETREATMENT ON THE HYDROCRACKING PERFORMANCE OF CATALYST "A" AT TWO LEVELS OF 315°C+ GAS-OIL CONVERSION

	60 wt% Conv. (LHSV = 0.5 h^{-1})		85 wt% Conv. (LHSV = 0.25 h^{-1})	
	SGO*	DSGO	SGO	DSGO
Conversion, wt%	60	60	82.2	84.5
Temperature, °C	413	400	415	400
Sulfur in TLP, ppm	50	11	n.d.	0
Nitrogen in TLP, ppm	~5	0.5	1	0
Yields, vol/vol of feed				
Naphtha (IBP-195°C)	25	33	45	55.5
Distillate (195-315°C)	39	35	45	37
Distillate/Naphtha ratio	1.5	1.0	1.0	0.7
Naphtha N+2A, vol%	75	75	72	69
Distillate Composition, vol%				
Paraffin	13	13	14	19
Cycloparaffin	54	68	57	75
Aromatic	33	19	28	5

* Values were interpolated from the data reported in Table 9B

n.d.: not determined

TABLE 11

PRODUCTION RUNS

Run	A	B	C
Feed SGO/DSGO, vol/vol	0/100	30/70	100/0
Aver. Bed Temperature, oC	408	408	408
Feed SGO/DSGO Vol/Vol	0/100	30/70	100/0
Pressure, psi	2750	2750	2750
H2/Feed Ratio, SCFB	5000	5000	5000
Nitrogen in feed, ppm	391	780	1665
Mass balance, wt%			
Gas	2.0	0.4	1.5
Naphtha (IBP-195 oC)	39.3	26.0	18.6
Light Distillate (195-290 oC)	29.8	26.4	18.7
Heavy Distillate (290-315 oC)	7.4	7.1	7.4
Gas-Oil (315 oC+)	21.5	40.1	53.8
H2 Consumption, SCFB	781	1015	1102
Liquid Volume Yields, 100*vol/vol of feed			
Naphtha (IBP-195 oC)	48.4	31.9	22.8
Light Distillate (195-290 oC)	33.1	29.1	20.5
Heavy Distillate (290-315 oC)	8.1	7.7	8.0
Gas-Oil (315 oC+)	23.2	43.1	57.6
Total Liquid Yield	112.8	111.8	108.9
Distillates/Naphtha ratio	0.85	1.15	1.25

TABLE 12

PRODUCTION RUNS - NAPHTHA (IBP-195 oC) QUALITY

Run	A	B	C
Density @15oC, kg/L	0.7515	0.7587	0.7688
API Gravity	56.7	54.9	52.5
Reid Vapor Pressure, Kpa	22.8	28.0	30.4
Sulfur, wt%	<.002	<.002	0.0118
H2S, ppm	<1	<1	<1
Mercaptans, ppm	2	2	6
Nitrogen total, ppm	1.2	0.3	2.4
ASTM Distillation ,% recovered at Vol.%			
IBP	41	44	40
10%	76	83	87
30%	106	112	115
50%	128	131	135
70%	152	149	157
90%	173	171	178
FBP	194	187	193
% Recovery	99.0	99.0	99.0
Research Octane, clear	59	60.6	60.6
Motor Octane, clear	59	59.5	59.6
Light-Ends Analysis (GLC+MS), Vol%			
C3	0.04	0.09	0.22
ic4	1.14	0.92	0.88
nC4	1.81	1.65	2.03
iC5	4.99	3.60	2.79
nC5	3.10	2.56	2.65
C6 paraffins	8.23	6.26	4.98
Cyclopentane	0.48	0.46	0.53
C6 cycloparaffins	5.88	6.96	6.91
Benzene	0.18	0.21	0.42
C7 +	74.15	77.29	78.59
PNA Analysis (GLC+MS), Vol% of C6+ fraction			
Paraffins	31.10	27.02	22.61
iso/normal	3.0	2.6	2.4
Naphtenes	65.21	70.18	71.20
Aromatics	3.69	2.79	6.19
N + 2A	72.6	75.8	83.6

TABLE 13

PRODUCTION RUNS - LIGHT DISTILLATE (195-290 oC) QUALITY

Run		CGSB Jet A	A	B	C
	Methods				
Density @15oC, kg/L	D4052	0.839 (max)	0.8331	0.8446	0.8593
API Gravity	D4052		38.3	36.0	33.1
Sulfur, wt%	XRF	0.2 (max)	0.0025	0.0016	0.0074
H2S, ppm	PCM118		<1	<1	<1
Mercaptans, ppm	PCM118	30 (max)	4	7	23
Nitrogen total, ppm	D3431		7.2	1.9	6.4
Aniline point, oC	D611		68.2	64.1	58
Smoke point, mm	D1322	20 (min) *	25.6	21.7	18.6
Pour point, oC	D97		<-66	<-66	<-66
Cloud point, oC	D2500		-71	-71	-71
Freezing point, Winter oC		-47 (max)			
Flash point, oC		38 (min)	88	86	92
Viscosity @-20oC, cSt	D445	8 (max)	10.67	11.72	18.60
Cetane number	D613		47.2	44.5	41.8
ASTM Distillation ,% recov. at,Vol%	D86				
IBP			216	208	218
10%		204 (max)	224	223	231
30%			230	230	237
50%			238	241	246
70%			251	254	258
90%			268	271	272
FBP		300 (max)	277	280	282
% Recovery			98.0	98.5	99.0
Hydrocarbon Analysis (MS), wt%					
Paraffins			15.02	9.34	8.91
Cycloparaffins			77.08	81.23	76.39
Aromatics, total			7.9	9.43	14.7
mono-			6.36	8.34	13.46
di-			1.53	1.09	0.44
tri-			0.01	0.01	0.79

* with naphtalenes content less than 3 vol% (otherwise Smoke point min. spec. is 25 mm)

TABLE 14

PRODUCTION RUNS - HEAVY DISTILLATE (290-315 oC) QUALITY

Run		CGSB Diesel A	A	B	C
	Methods				
Density @15oC, kg/L	D4052		0.8485	0.8609	0.8763
API Gravity	D4052		35.2	32.8	29.9
Sulfur, wt%	XRF	0.5 (max)	0.0032	0.0017	0.006
H2S, ppm	PCM118		<1	<1	<1
Mercaptans, ppm	PCM118		7	10	16
Nitrogen total, ppm	D3431		10.1	3.7	6.5
Aniline point, oC	D611		82.7	78.0	70.7
Smoke point, mm	D1322		24.5	N/A	16.8
Pour point, oC	D97	-39 (max)	-39	-42	-44
Cloud point, oC	D2500	-34 (max)	-40	-42	-44
Flash point, oC		40 (min)	150	147	151
Viscosity @-20oC, cSt	D445		68.90	84.40	109.80
Cetane number	D613		58.0	53.5	50.3
ASTM Distillation ,% recov. at,vol%	D86				
IBP			292	293	295
10%			298	297	298
30%			299	298	299
50%			300	299	300
70%			302	301	303
90%		315 (max)	305	305	307
FBP			309	309	312
% Recovery			99.0	98.8	99.0
Hydrocarbon Analysis (MS), wt%					
Paraffins			13.66	8.83	6.82
Cycloparaffins			68.43	73.94	71.03
Aromatics, total			17.9	17.23	22.15
mono-			7.03	8.81	12.78
di-			7.68	4.66	4.01
tri-			2	2.49	3.69
tetra-			0.28	0.22	0.25
Aromatics, sulfur			0.91	1.06	1.42

TABLE 15

PRODUCTION RUNS - GAS-OIL (315 oC +) INSPECTION

Run	Methods	A	B	C
Density @15oC, kg/L	D4052	0.8571	0.8665	0.8820
API Gravity	D4052	33.5	31.7	28.8
Sulfur, wt%	XRF	0.005	<.002	0.006
Nitrogen total, ppm	D3431	16.3	3.5	7.5
Conradson Carbon, wt%	D189	0.024	0.009	0.027
Pour point, oC	D97	-9	3	-3
Viscosity @65oC, cSt	D445	6.95	8.62	11.15
Hydrocarbon Analysis (MS), Wt%				
Paraffins		27.84	15.56	12.62
Cycloparaffins		65.94	77.58	76.67
mono-		28.95	23.27	18.51
di-		21.38	27.03	26.09
tri-		9.35	15.43	17.06
tetra-		4.93	8.46	10.30
penta-		1.33	3.40	4.71
Aromatics, total				
mono-		3.35	3.88	6.15
di-		1.18	1.53	2.64
tri-		0.35	0.36	0.57
tetra-		0.42	0.37	0.44
penta-		0.00	0.04	0.05
Aromatics, sulfur		0.31	0.27	0.45
Others		0.60	0.40	0.40

TABLE 16

HIGH SEVERITY TEST - KINETIC STUDY OF 315°C+ GAS OIL CONVERSION

Temp. (°C)	1/SV (h)	1st-Order Rate - SGO Y_{GO}, wt%			2nd-Order Rate - SGO Y_{GO}, wt%			2nd-Order Rate - DSGO Y_{GO}, wt%		
		obs.	calc.	delta	obs.	calc.	delta	obs.	calc.	delta
400	1.0	84.7	85.1	+0.4	84.7	82.8	-1.9	40.7	40.8	+0.1
	2.0	73.2	73.2	0.0	73.2	71.3	-2.0	39.1	27.3	-11.8
	4.0	47.1	51.0	+3.9	47.1	53.5	+6.4	15.5	15.1	0.4
408	1.0	69.0	74.4	+5.4	69.0	69.1	+0.1	21.0	20.1	-0.9
	2.0	57.7	55.3	-2.4	57.7	52.7	-5.0	11.9	11.7	-0.2
	4.0	39.7	29.9	-9.8	39.7	35.4	-4.4	5.3	5.9	+0.6
415	1.0	53.9	60.3	+6.4	53.9	53.3	-0.6	8.7	9.4	+0.7
	2.0	33.7	36.7	+3.0	33.7	36.6	+2.9	5.0	5.3	+0.3
	4.0	17.8	12.5	-5.3	17.8	21.7	+3.9	2.5	2.6	+0.1
Sum of squares of residuals				225			115			141

SGO - 1st-order kinetics $Y_{GO} = 100 \exp [8.45\ 10^{21} \exp (-35{,}200 /T) \times t]$

SGO - 2nd-order kinetics $Y_{GO} = 1/[0.01 + 8.24\ 10^{25} \exp (-44{,}310 /T) \times t]$

DSGO - 2nd-order kinetics $Y_{GO} = 1/[0.01 + 1.16\ 10^{36} \exp (-58{,}750 /T) \times t]$

T: Temperature (°K)
t: time (h)

TABLE 17

k VALUES OF PSEUDO FIRST-ORDER KINETICS FOR DIFFERENT HYDROCARBON TYPES IN SYNCRUDE GAS OIL

	SGO/400°C	SGO/408°C	SGO/415°C	DSGO/400°C
Poly-Aromatic Hydrocarbons (PAH)	0.45	0.56	0.94	1.10
Mono-Aromatic Hydrocarbons (MAH)	0.08	0.37	0.76	1.0
Poly-Cyclo-Paraffins (PCP)	0.06	0.19	0.33	0.52
Mono-Cyclo-Paraffins (MCP)	0.05	0.14	0.41	0.24
Paraffins (Par)	0.09	0.16	0.07	0.09

TABLE 18

DISTILLATE YIELD PREDICTION - TRIANGULAR MODEL

SGO

Temp. (°C)	k_0	$K_1=k_1/k_0$	$K_2=k_2/k_0$	k_1	k_2
400	0.21	0.635	0.0	0.133	0
408	0.456	0.620	0.054	0.283	0.025
415	0.882	0.703	0.106	0.620	0.093

	1/SV (h)	Observed Yield wt%	Calculated Yield wt%	Delta
400	1.0	10.96	10.96	0.0
	2.0	17.04	18.23	+1.2
	4.0	30.19	29.5	-0.7
408	1.0	21.91	18.91	-3.0
	2.0	25.42	28.42	+3.0
	4.0	38.25	37.57	-0.7
415	1.0	30.33	31.01	+0.7
	2.0	40.38	39.48	-0.9
	4.0	41.33	40.96	+0.4

TABLE 19

DISTILLATE YIELD PREDICTION - TRIANGULAR MODEL

DSGO

Temp. (°C)	k_{0}-	$K_1=k_1/k_{0}$-	$K_2=k_2/k_{0}$-	k_{1}-	k_{2}-
400	1.4	0.55	0.080	0.78	0.11
408	4.0	0.53	0.031	2.12	0.12
415	9.5	0.43	0.015	4.1	0.15

	1/SV (h)	Observed Yield wt%	Calculated Yield wt%	Delta
400	1.0	31.0	30.30	-0.7
	2.0	33.6	34.50	+0.9
	4.0	33.5	33.30	-0.2
408	1.0	36.5	38.7	+2.2
	2.0	41.9	38.9	-3.0
	4.0	31.8	32.8	+1.0
415	1.0	34.8	34.2	-0.6
	2.0	30.9	31.8	+0.9
	4.0	24.7	24.3	-0.4

FIG. 1: Microreactor System

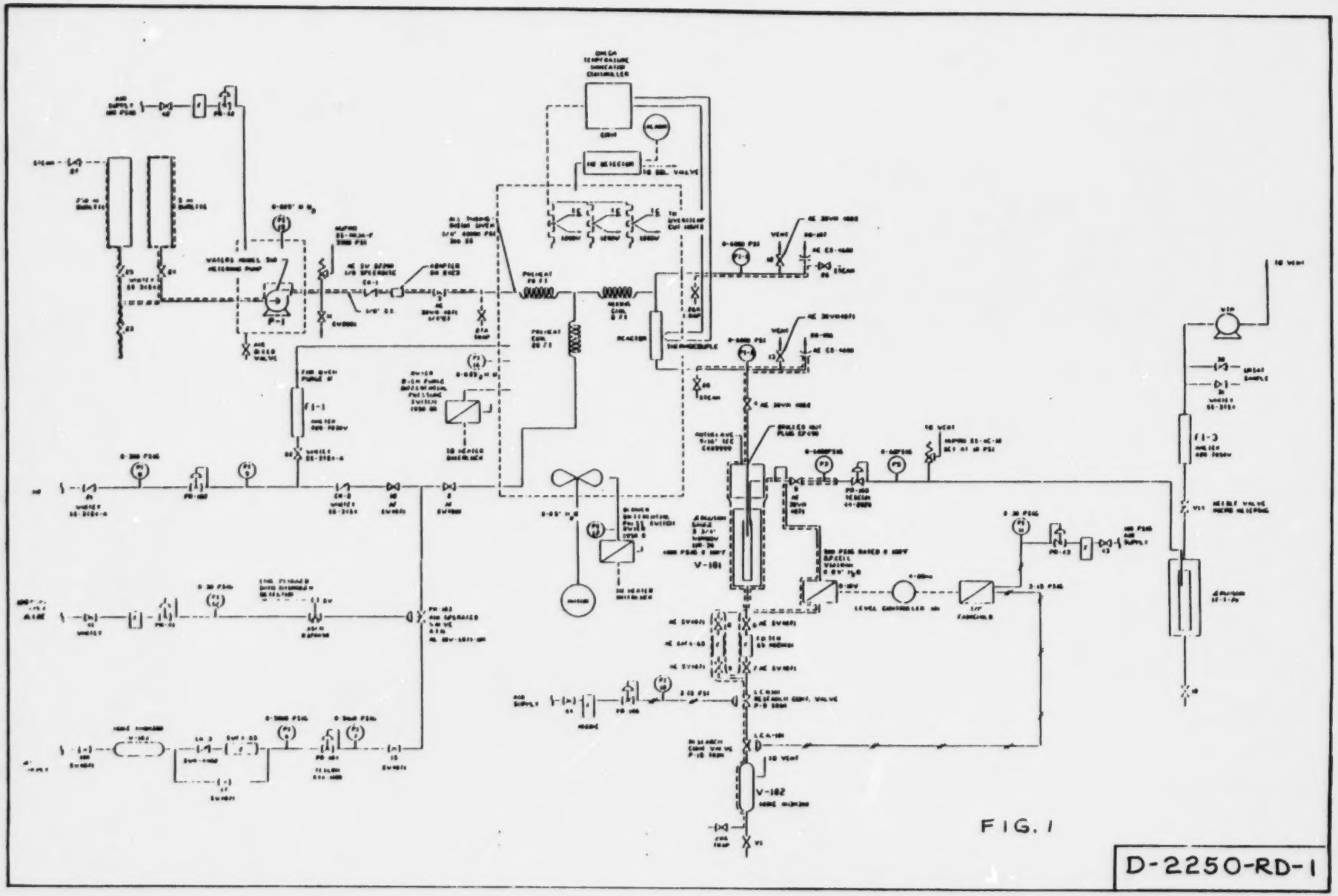


FIG. 1

D-2250-RD-1

FIG. 2: Petro-Canada PRD Reactor Unit

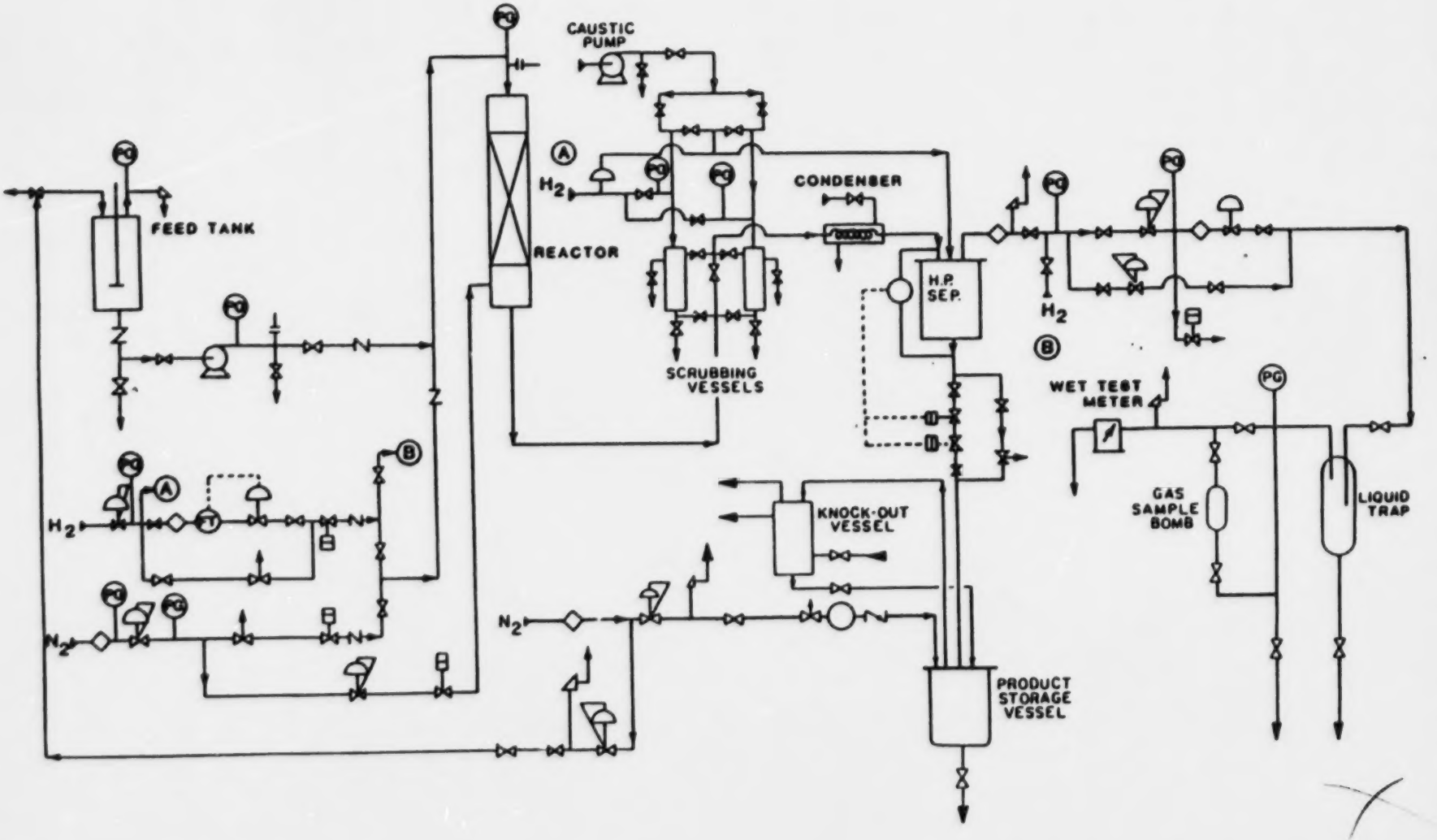


FIG 3:

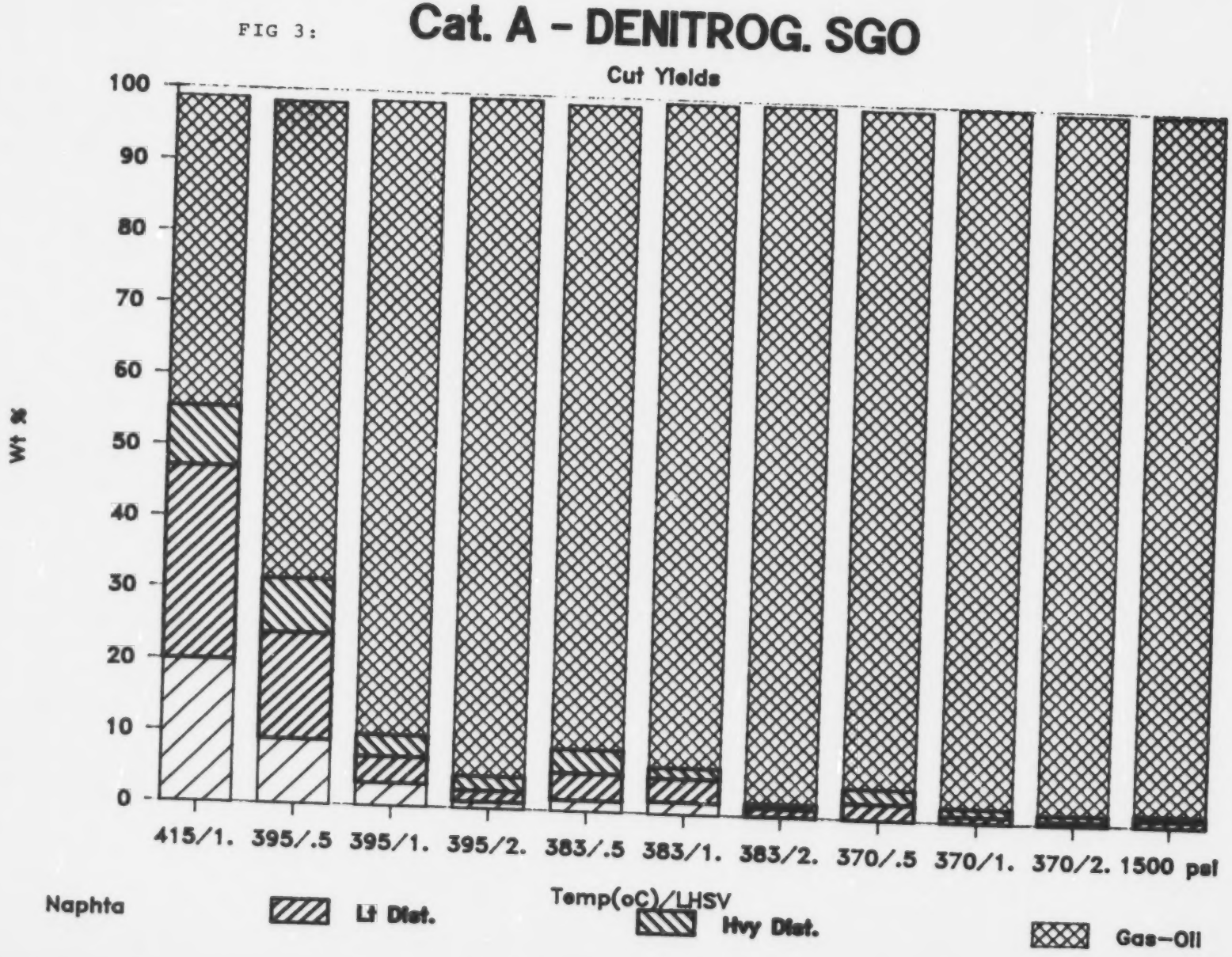

Cat. A - DENITROG. SGO
Cut Yields
Wt %
100
90
80
70
60
50
40
30
20
10
0
415/1.
395/.5
395/1.
395/2.
383/.5
383/1.
383/2.
370/.5
370/1.
370/2.
1500 psi
Temp(oC)/LHSV
Naphta
Lt Dist.
Hvy Dist.
Gas-Oil

FIG. 4:

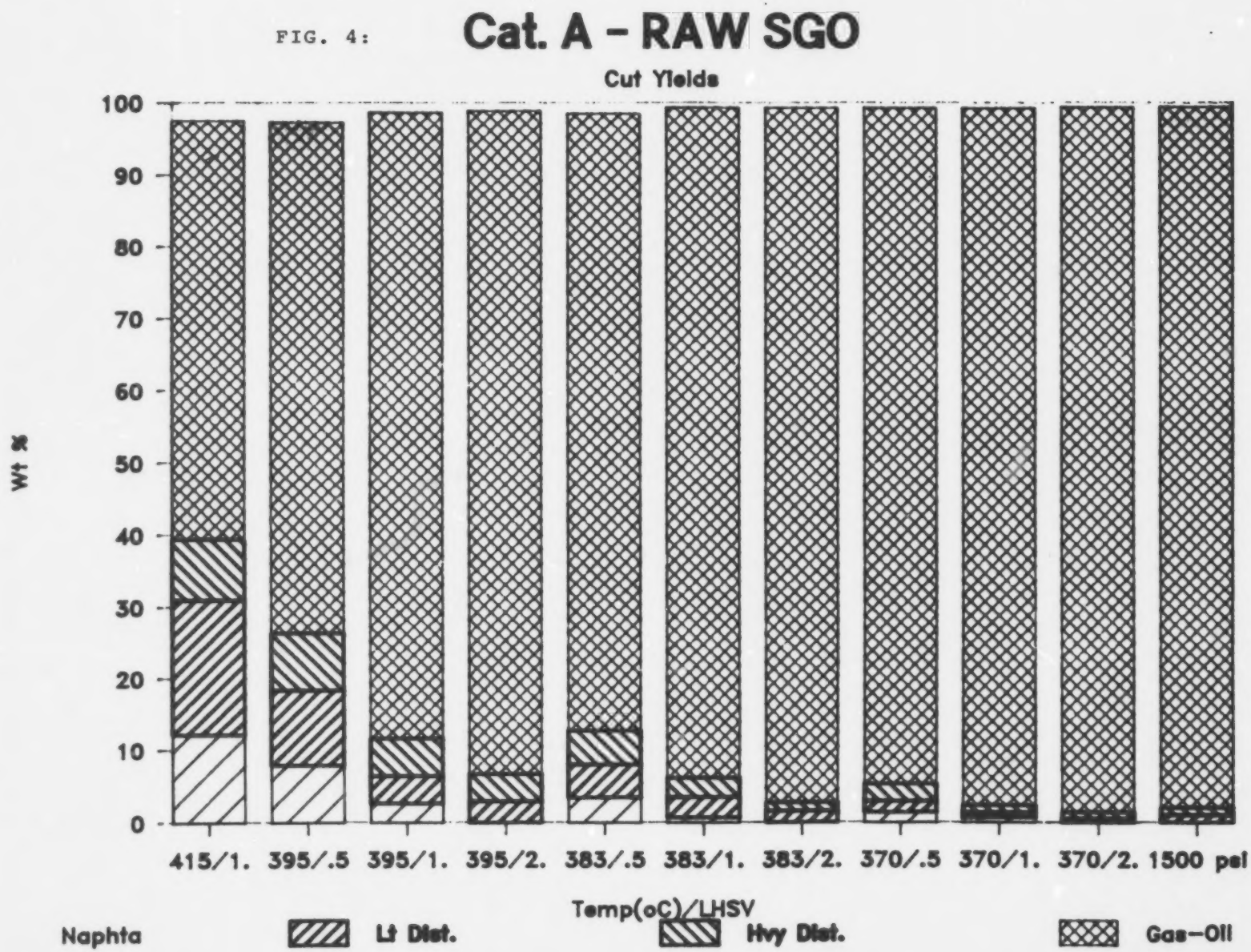

Cat. A - RAW SGO
Cut Yields
Wt %
100
90
80
70
60
50
40
30
20
10
0
415/1.
395/.5
395/1.
395/2.
383/.5
383/1.
383/2.
370/.5
370/1.
370/2.
1500 psi
Temp(oC)/LHSV
Naphta
Lt Dist.
Hvy Dist.
Gas-Oil

FIG.5:

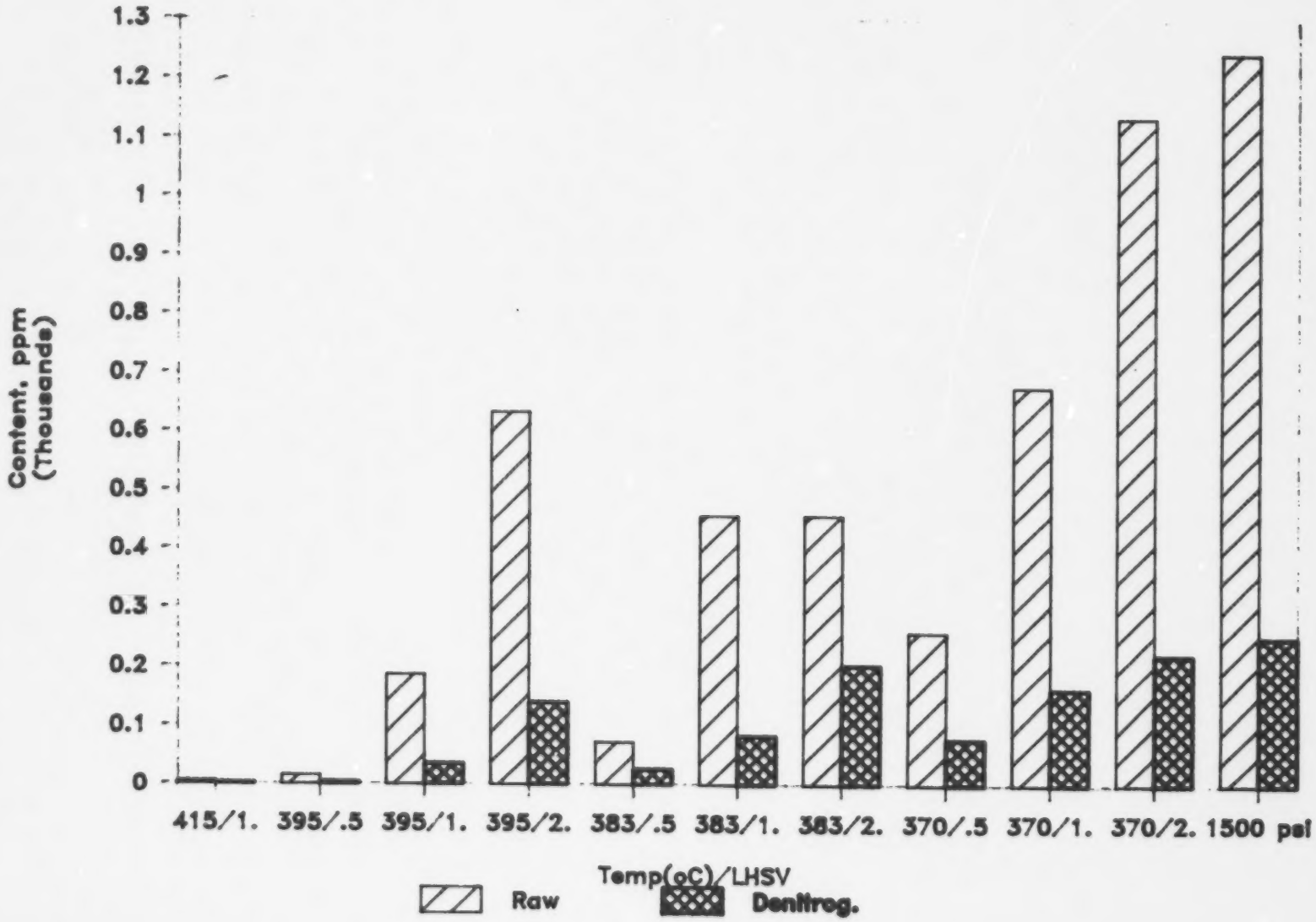

Cat. A - Nitrogen in TLP
Content, ppm (Thousands)
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
415/1.
395/.5
395/1.
395/2.
383/.5
383/1.
383/2.
370/.5
370/1.
370/2.
1500 psi
Temp(oC)/LHSV
Raw
Denitrog.

FIG. 6:

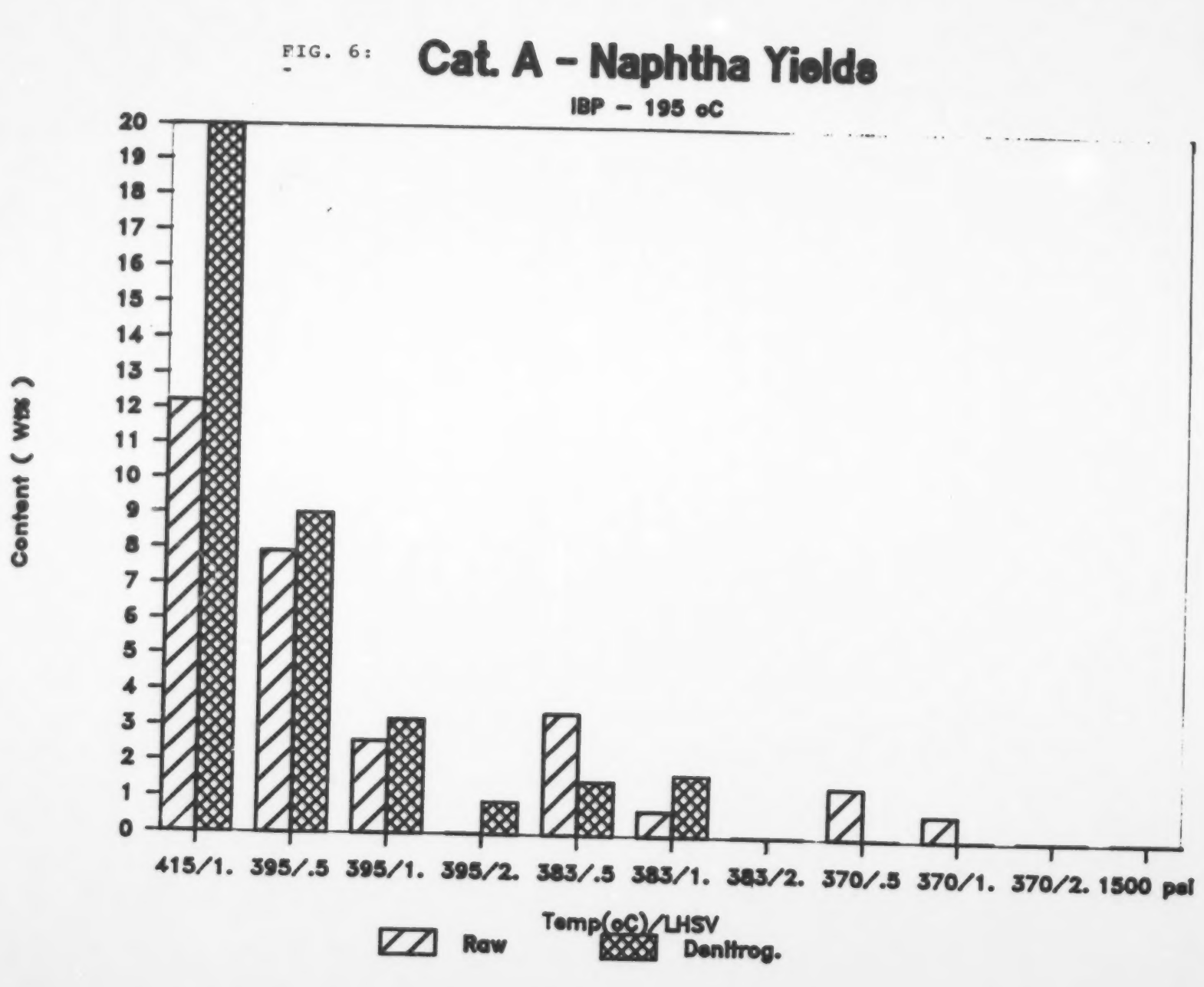

Cat. A - Naphtha Yields
IBP - 195 oC
Content (Wt%)
20
19
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
415/1.
395/.5
395/1.
395/2.
383/.5
383/1.
383/2.
370/.5
370/1.
370/2.
1500 psi
Temp(oC)/LHSV
Raw
Denitrog.

FIG. 7:

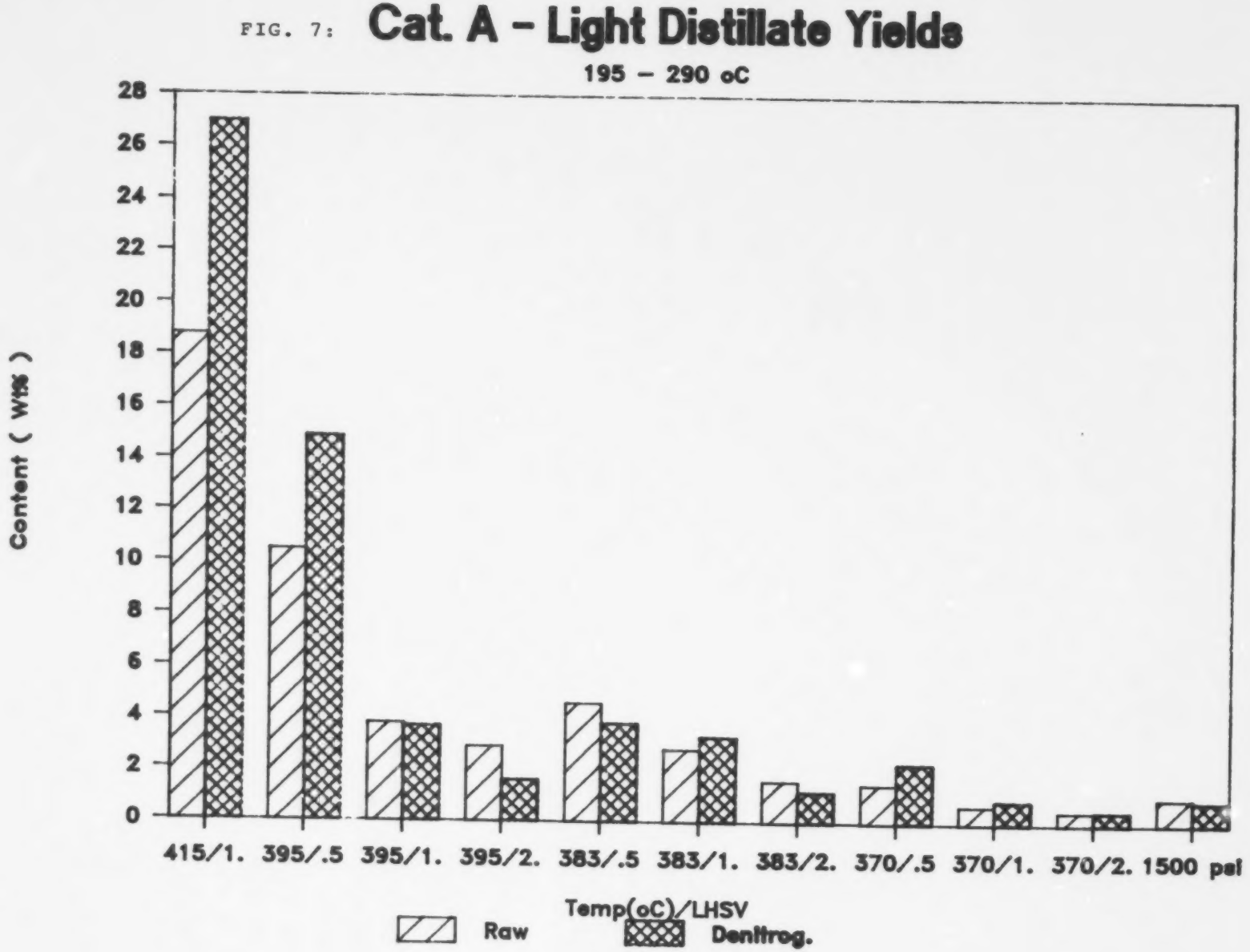

Cat. A – Light Distillate Yields
195 – 290 oC
Content (Wt%)
28
26
24
22
20
18
16
14
12
10
8
6
4
2
0
415/1.
395/.5
395/1.
395/2.
383/.5
383/1.
383/2.
370/.5
370/1.
370/2.
1500 psi
Temp(oC)/LHSV
Raw
Denitrog.

FIG. 8: **Cat. A - Heavy Distillate Yields**

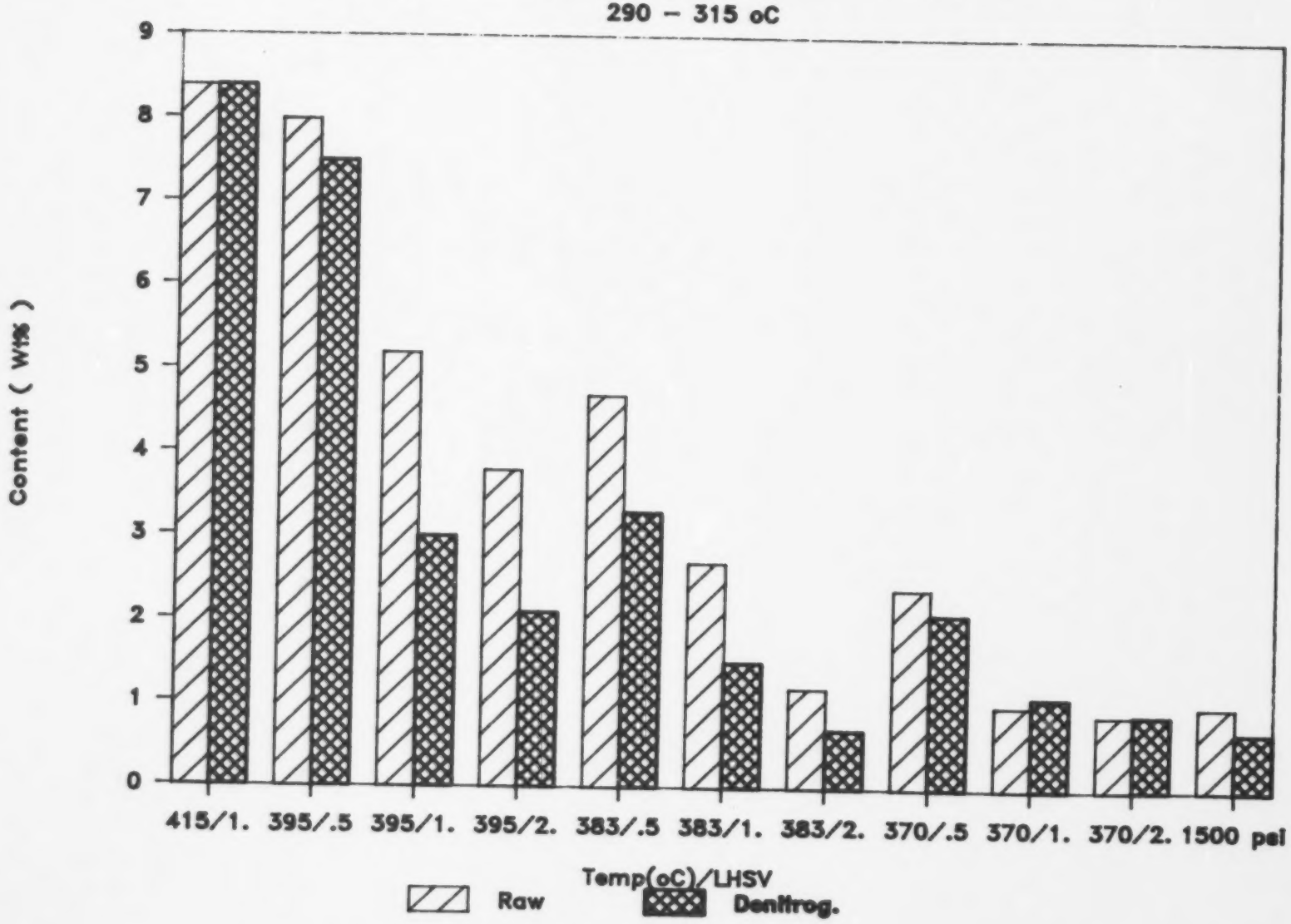


FIG. 9:

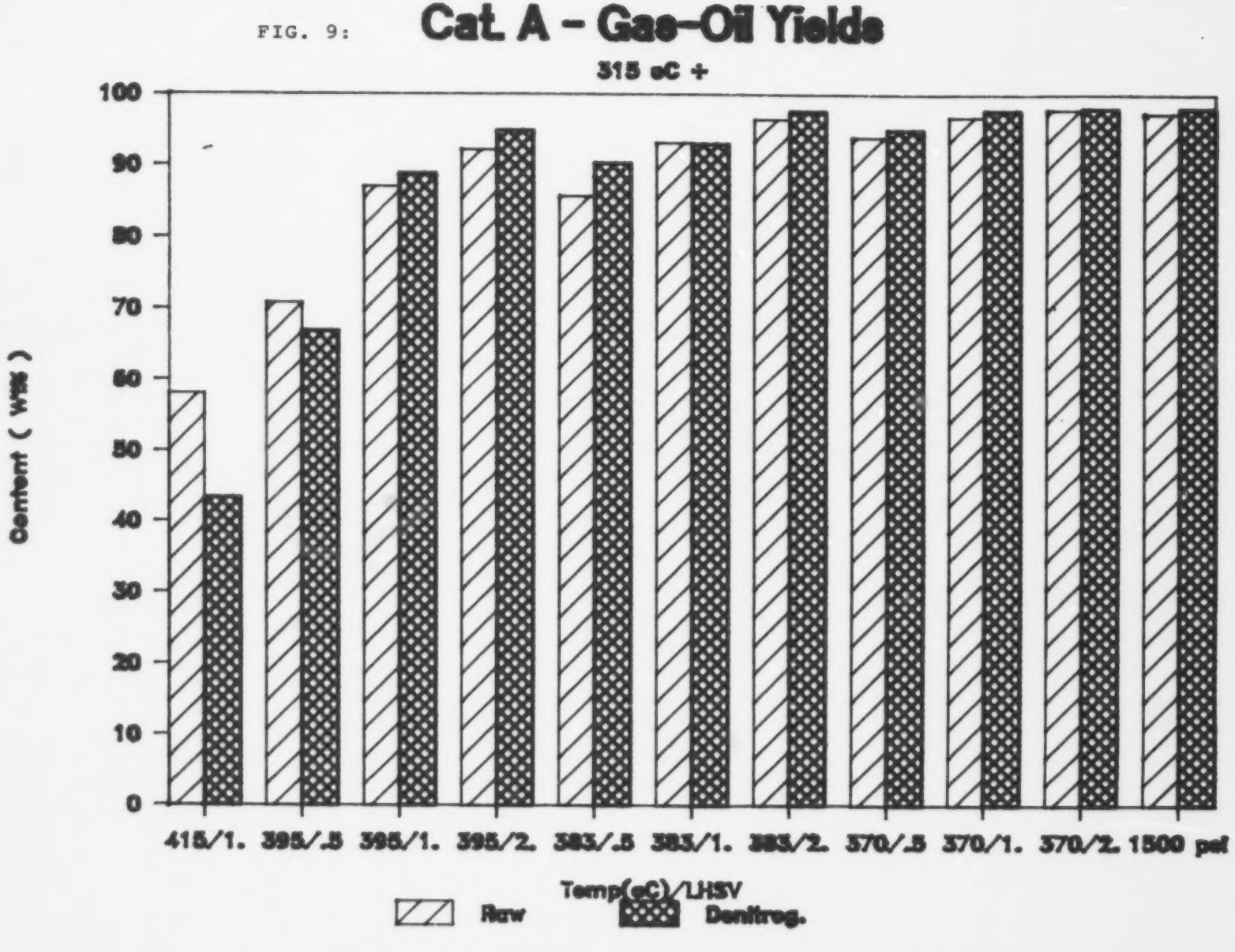

Cat. A - Gas-Oil Yields
315 oC +
Content (WT%)
100
90
80
70
60
50
40
30
20
10
0
415/1.
395/.5
395/1.
395/2.
383/.5
383/1.
383/2.
370/.5
370/1.
370/2.
1500 psi
Temp(oC)/LHSV
Raw
Denitrog.

FIG. 10:

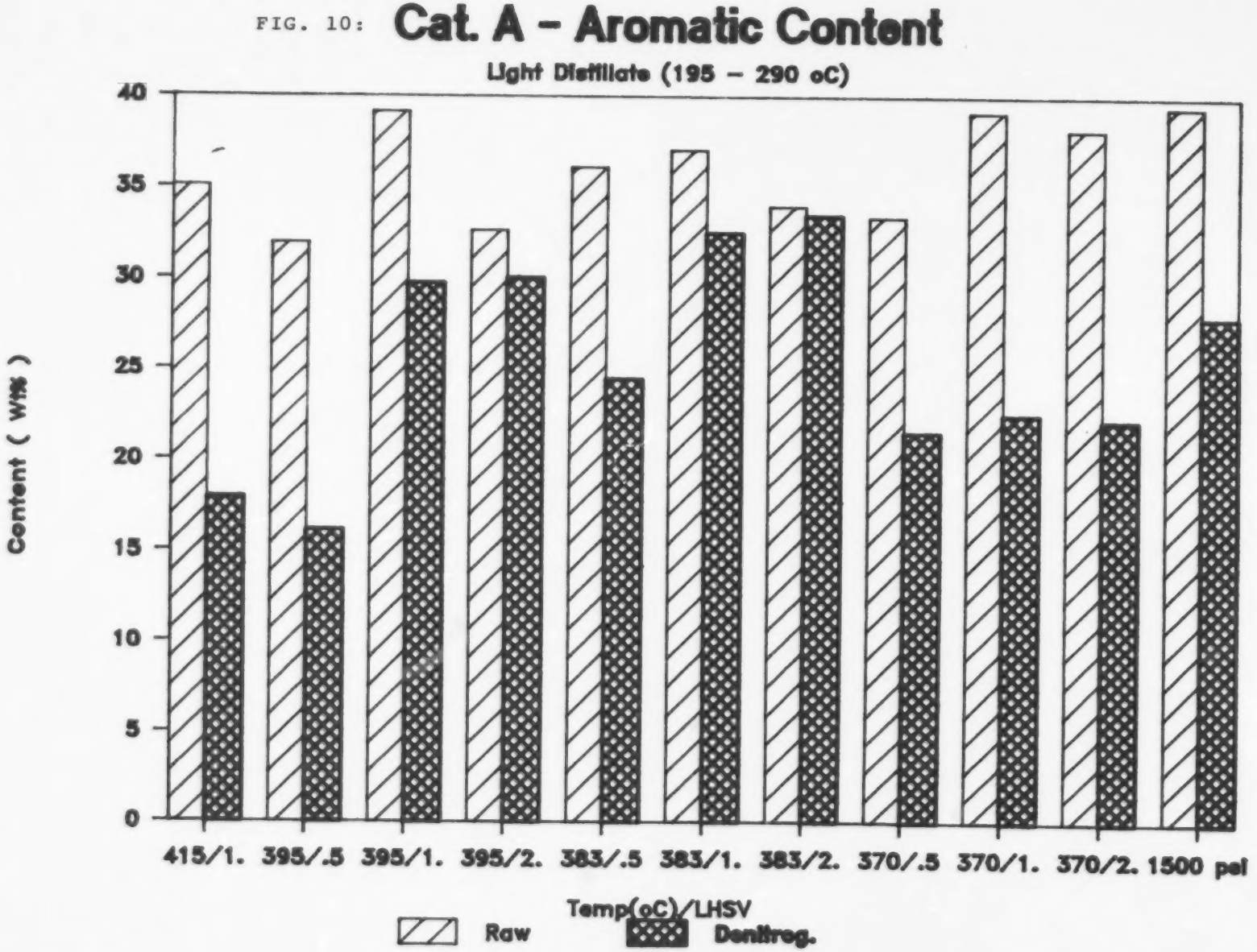

Cat. A - Aromatic Content
Light Distillate (195 - 290 oC)
Content (Wt%)
40
35
30
25
20
15
10
5
0
415/1.
395/.5
395/1.
395/2.
383/.5
383/1.
383/2.
370/.5
370/1.
370/2.
1500 psi
Temp(oC)/LHSV
Raw
Denitrog.

FIG. 11: **Cat. A - Cycloparaffin Content**

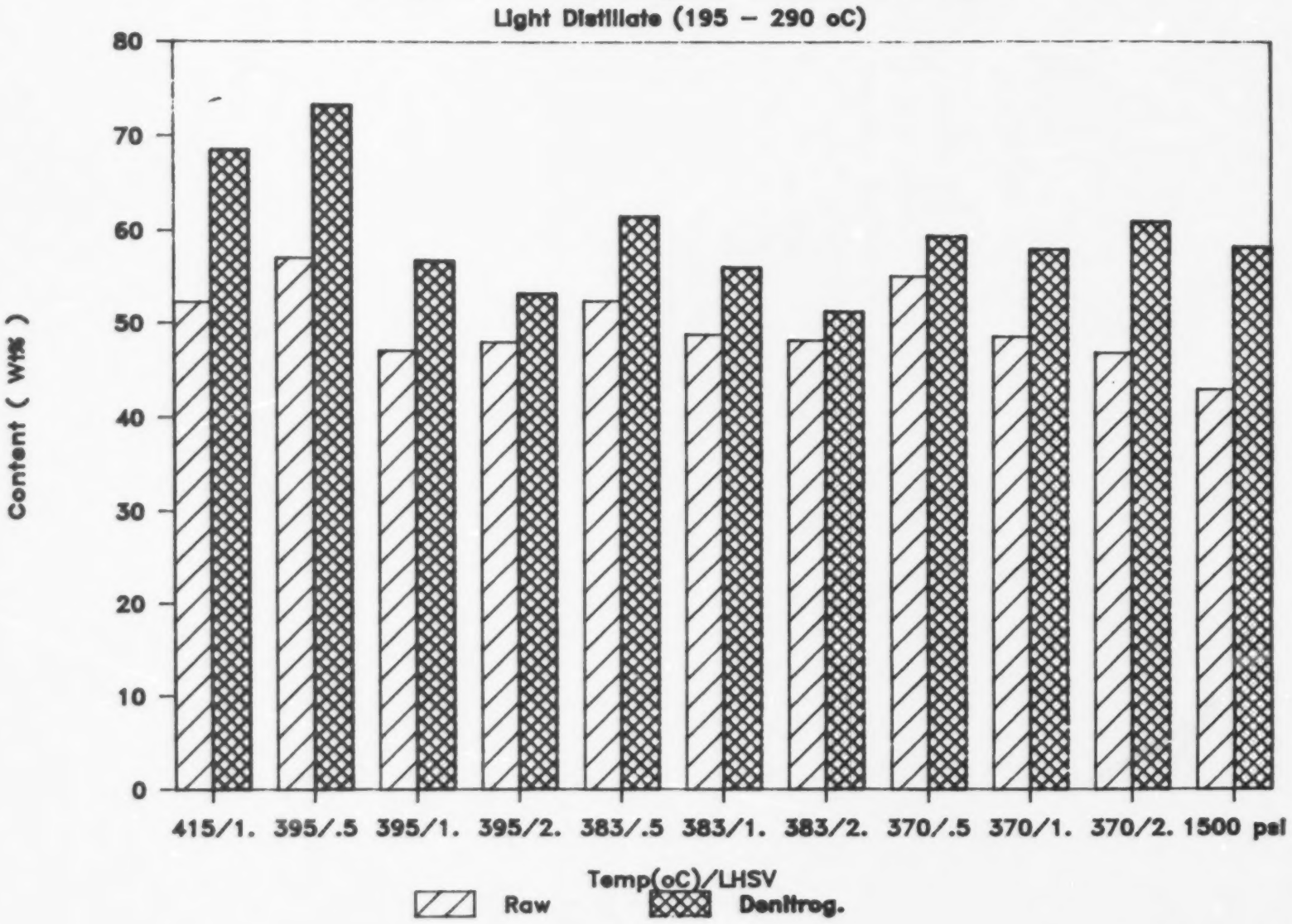


FIG. 12:

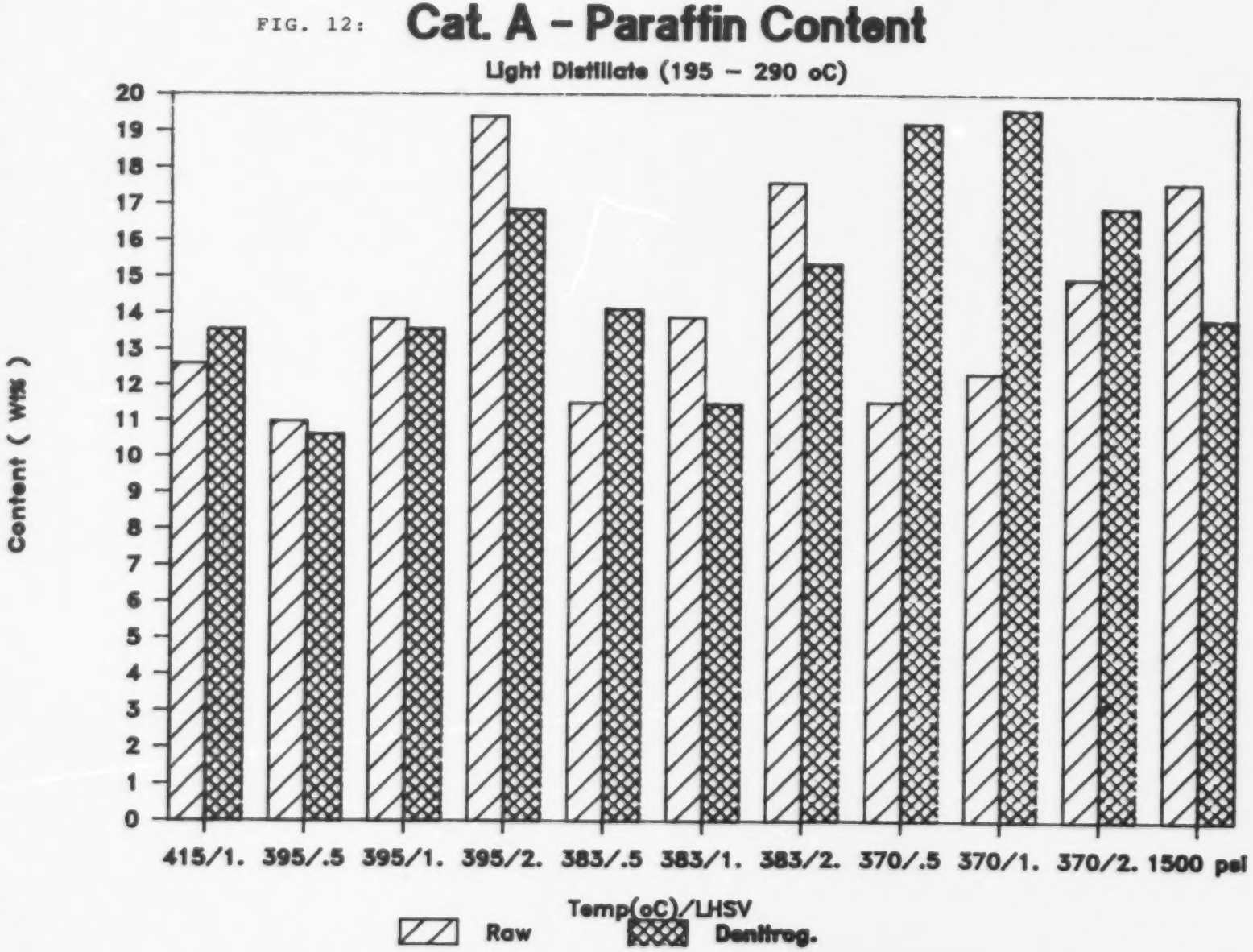

Cat. A - Paraffin Content
Light Distillate (195 - 290 oC)
Content (Wt%)
20
19
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
415/1.
395/.5
395/1.
395/2.
383/.5
383/1.
383/2.
370/.5
370/1.
370/2.
1500 psi
Temp(oC)/LHSV
Raw
Dentreg.

FIG. 13: **Cat. A – Aromatic content**

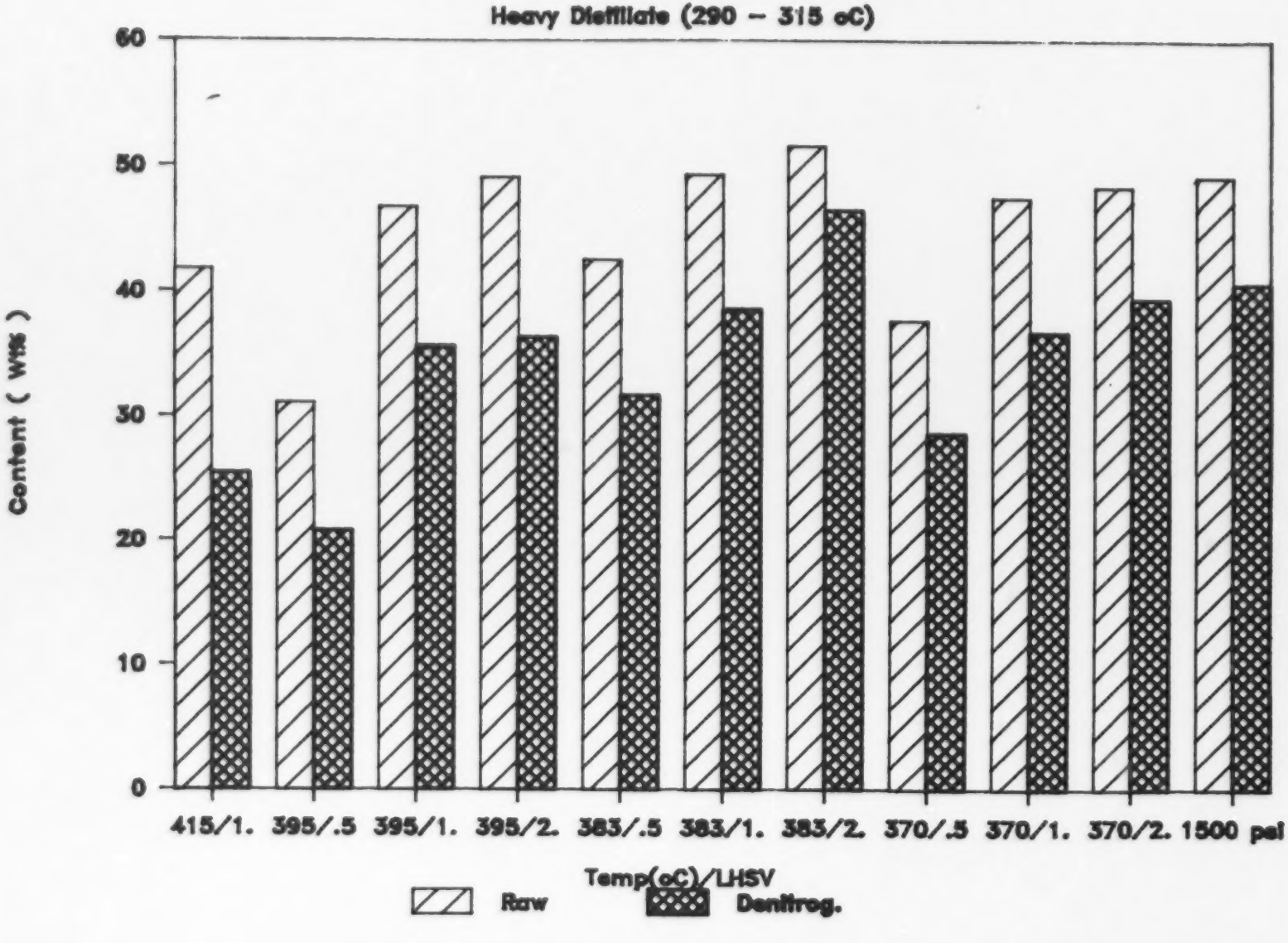


FIG. 14:

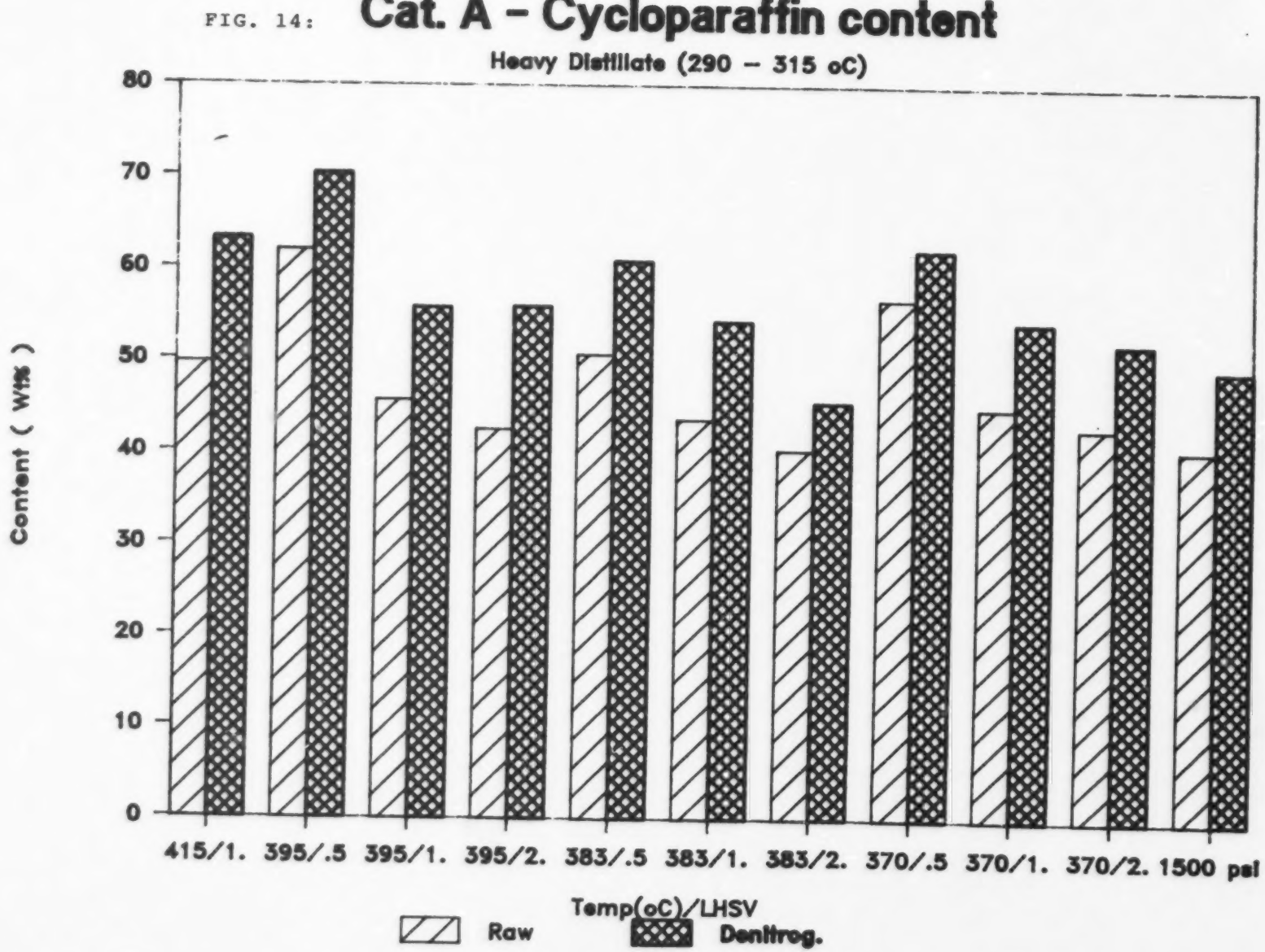

Cat. A - Cycloparaffin content
Heavy Distillate (290 - 315 oC)
Content (Wt%)
80
70
60
50
40
30
20
10
0
415/1.
395/.5
395/1.
395/2.
383/.5
383/1.
383/2.
370/.5
370/1.
370/2.
1500 psi
Temp(oC)/LHSV
Raw
Denitrog.

FIG. 15:

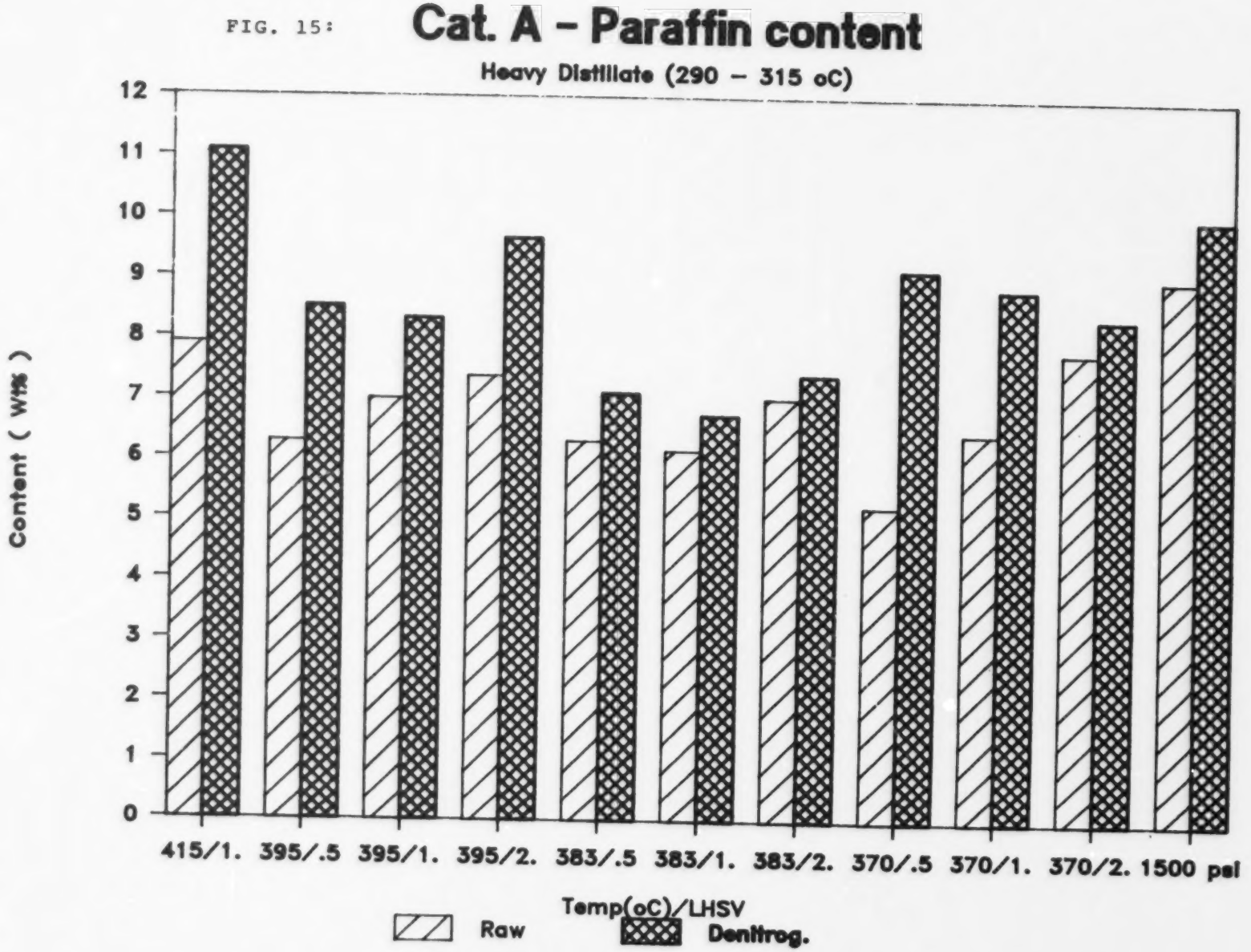

Cat. A - Paraffin content
Heavy Distillate (290 - 315 oC)
Content (Wt%)
12
11
10
9
8
7
6
5
4
3
2
1
0
415/1.
395/.5
395/1.
395/2.
383/.5
383/1.
383/2.
370/.5
370/1.
370/2.
1500 psi
Temp(oC)/LHSV
Raw
Denitrog.

FIG. 16:

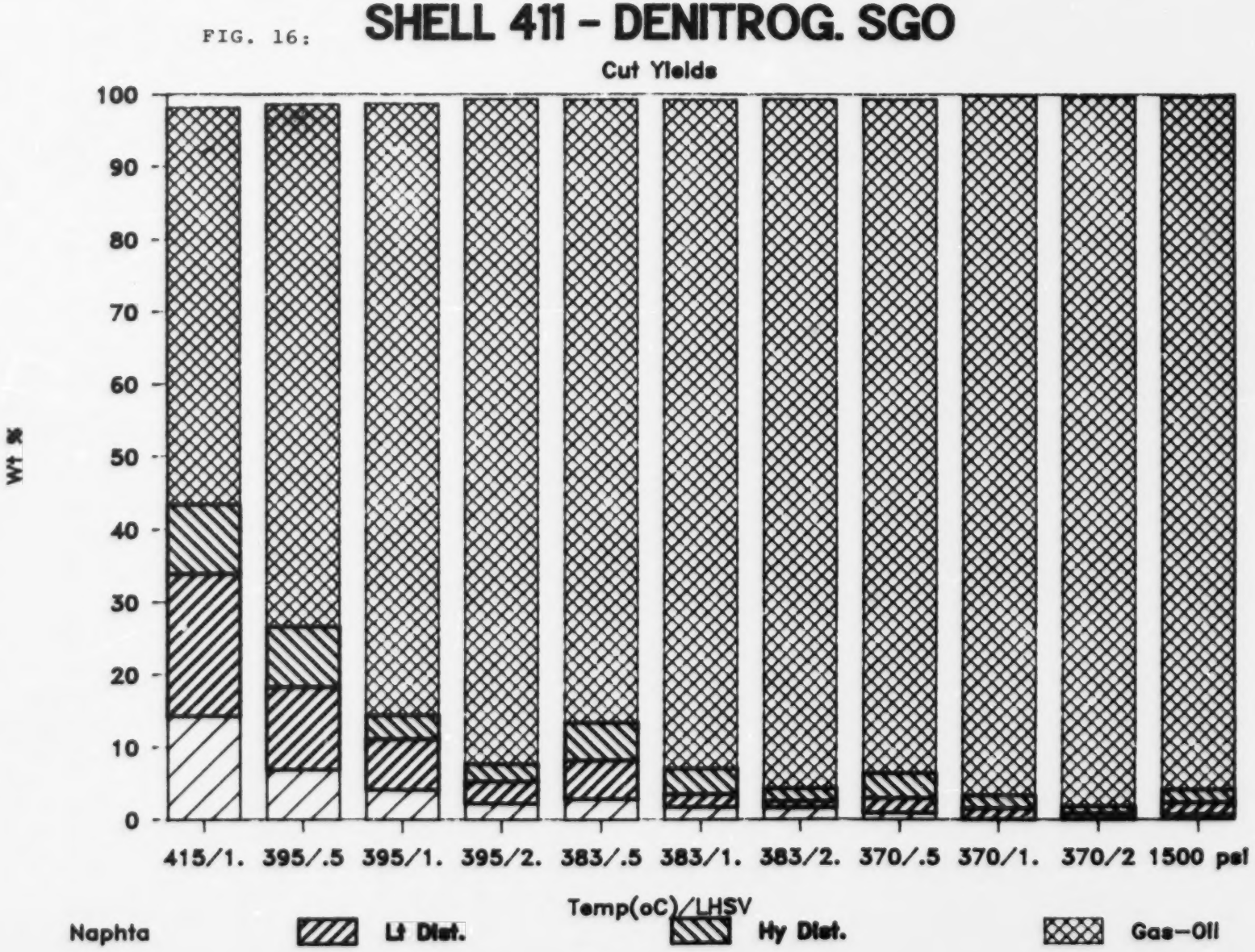

SHELL 411 - DENITROG. SGO
Cut Yields
Wt %
100
90
80
70
60
50
40
30
20
10
0
415/1.
395/.5
395/1.
395/2.
383/.5
383/1.
383/2.
370/.5
370/1.
370/2
1500 psi
Temp(oC)/LHSV
Naphta
Lt Dist.
Hy Dist.
Gas-Oil

FIG. 17:

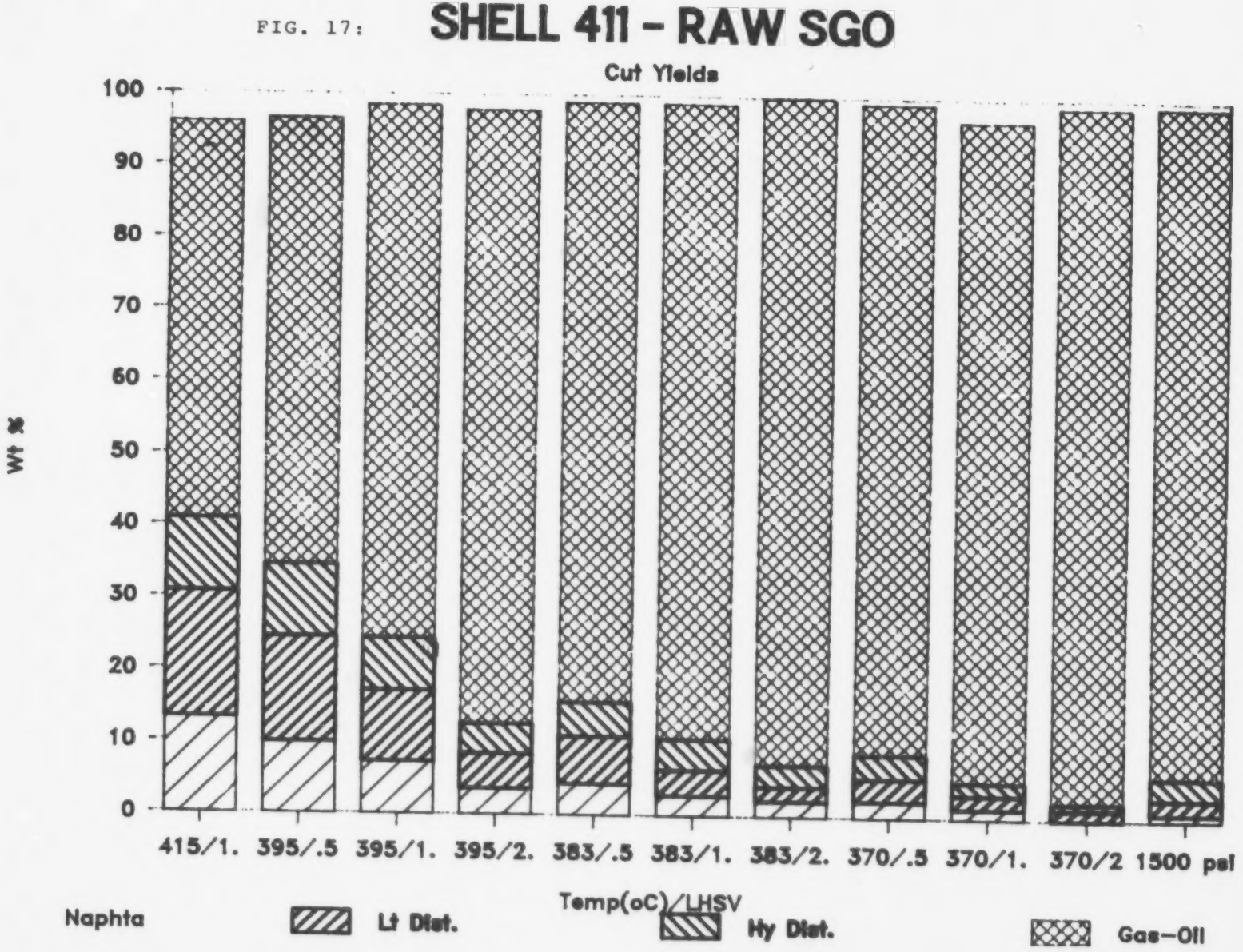

SHELL 411 - RAW SGO
Cut Yields
Wt %
100
90
80
70
60
50
40
30
20
10
0
415/1.
395/.5
395/1.
395/2.
383/.5
383/1.
383/2.
370/.5
370/1.
370/2
1500 psi
Temp(oC)/LHSV
Naphta
Lt Dist.
Hy Dist.
Gas-Oil

FIG. 18:

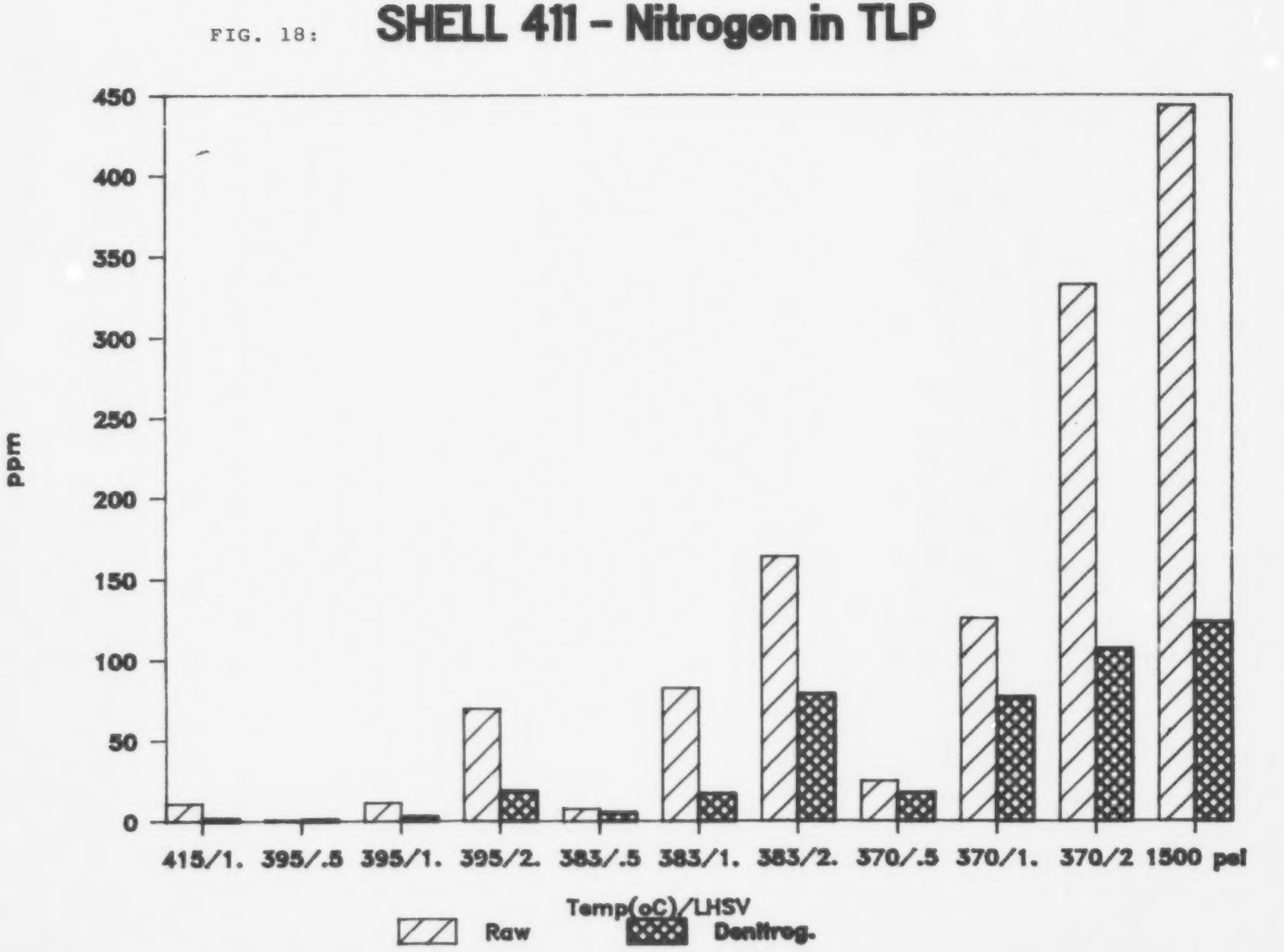

SHELL 411 - Nitrogen in TLP
ppm
450
400
350
300
250
200
150
100
50
0
415/1.
395/.5
395/1.
395/2.
383/.5
383/1.
383/2.
370/.5
370/1.
370/2
1500 psi
Temp(oC)/LHSV
Raw
Denitrog.

FIG. 19:

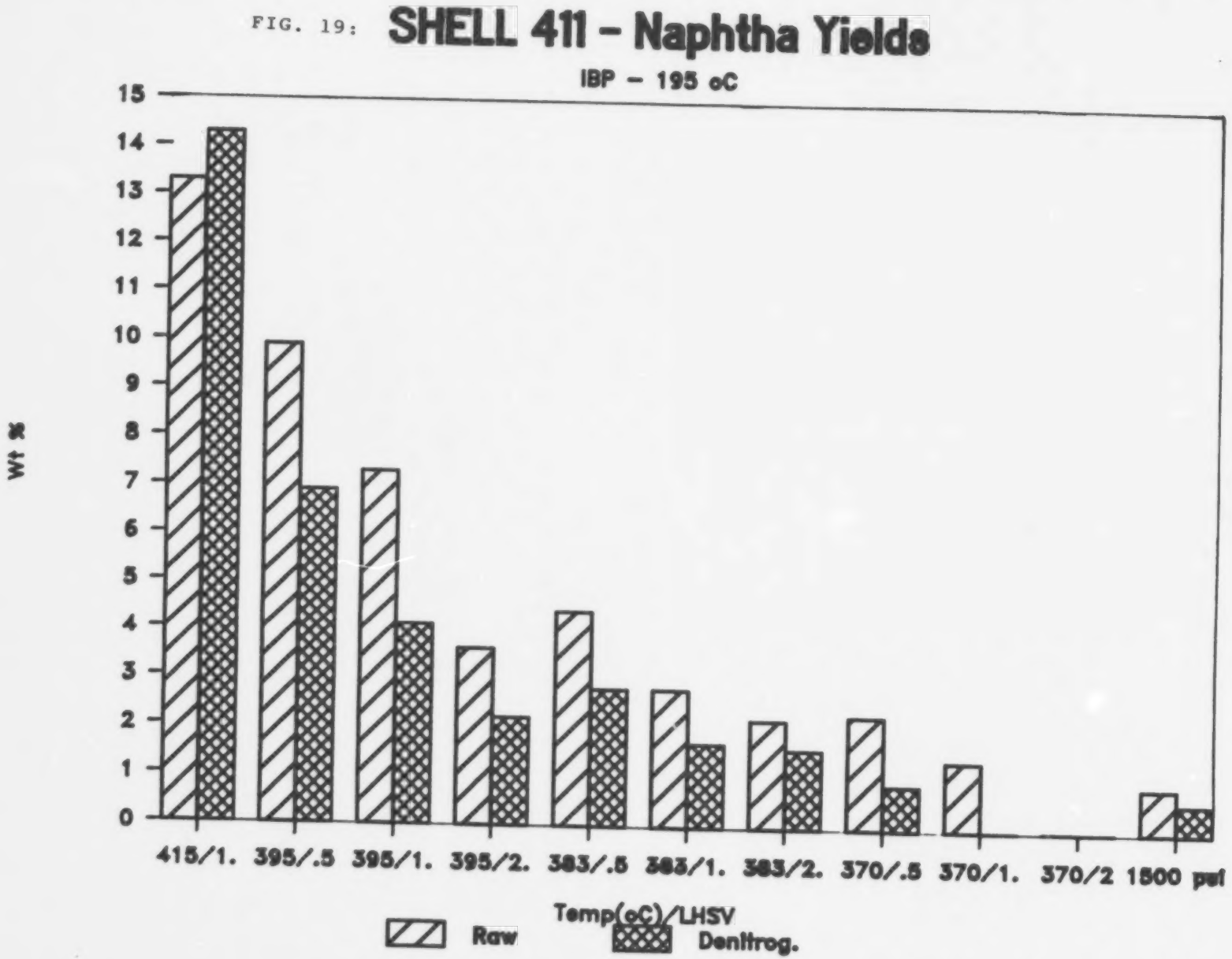

SHELL 411 - Naphtha Yields
IBP - 195 oC
Wt %
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
415/1.
395/.5
395/1.
395/2.
383/.5
383/1.
383/2.
370/.5
370/1.
370/2
1500 psi
Temp(oC)/LHSV
Raw
Denitrog.

FIG. 20:

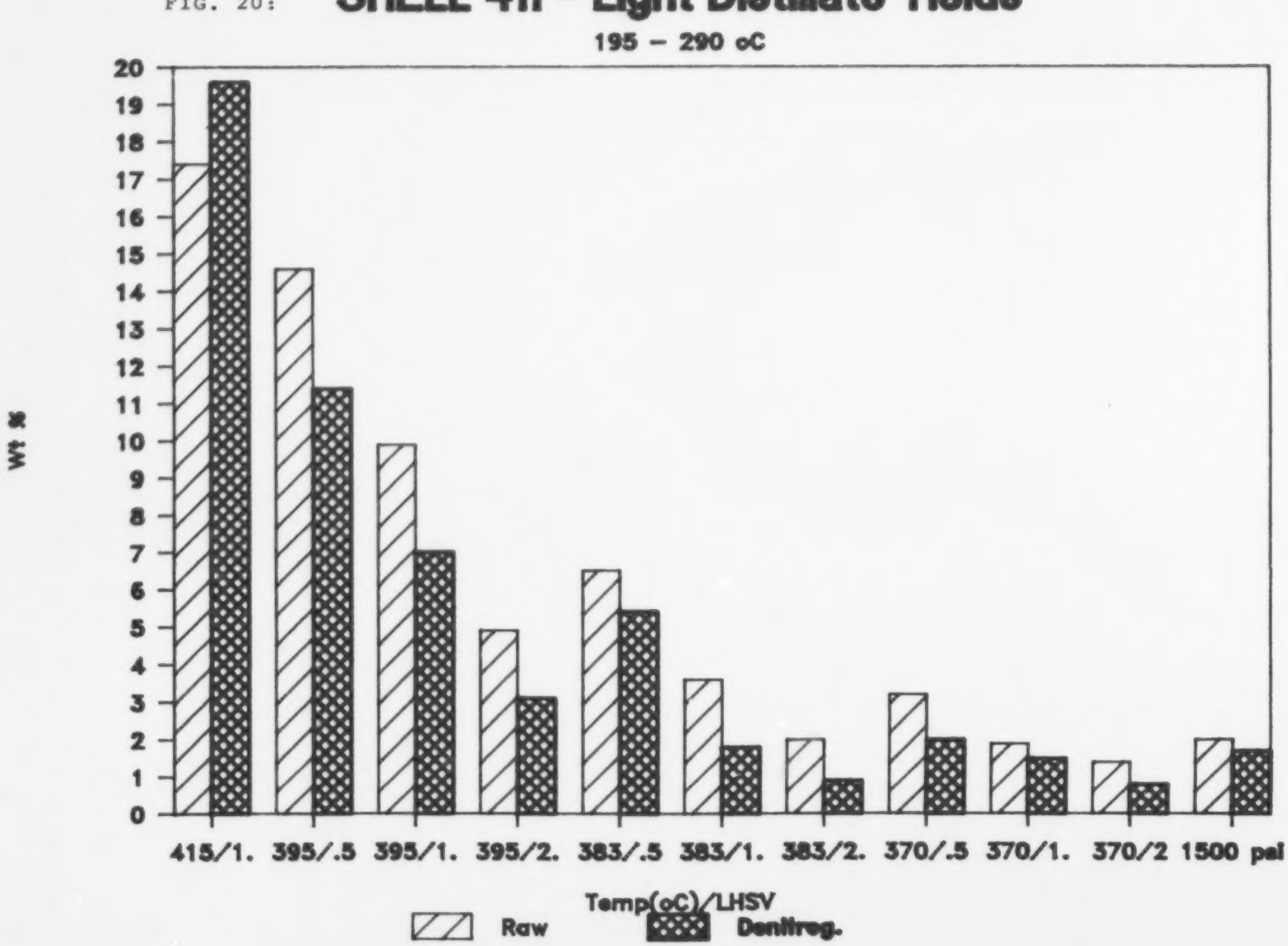

SHELL 411 - Light Distillate Yields
195 - 290 oC
Wt %
20
19
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
415/1.
395/.5
395/1.
395/2.
383/.5
383/1.
383/2.
370/.5
370/1.
370/2
1500 psi
Temp(oC)/LHSV
Raw
Dentreg.

FIG. 21:

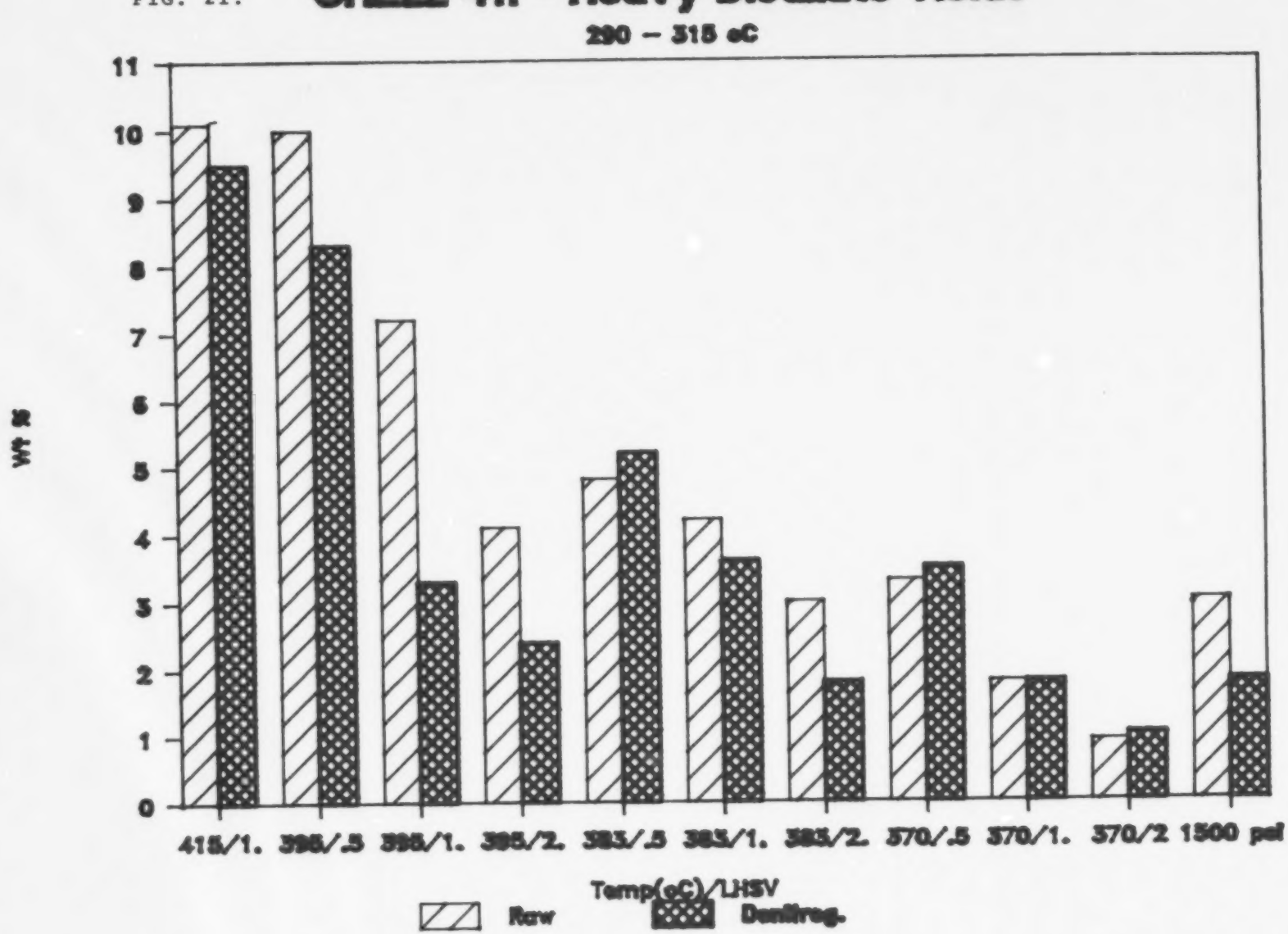

SHELL 411 - Heavy Distillate Yields
290 - 315 oC
Wt %
11
10
9
8
7
6
5
4
3
2
1
0
415/1.
395/.5
395/1.
395/2.
385/.5
385/1.
385/2.
370/.5
370/1.
370/2
1500 psi
Temp(oC)/LHSV
Raw
Dewax.

FIG. 22:

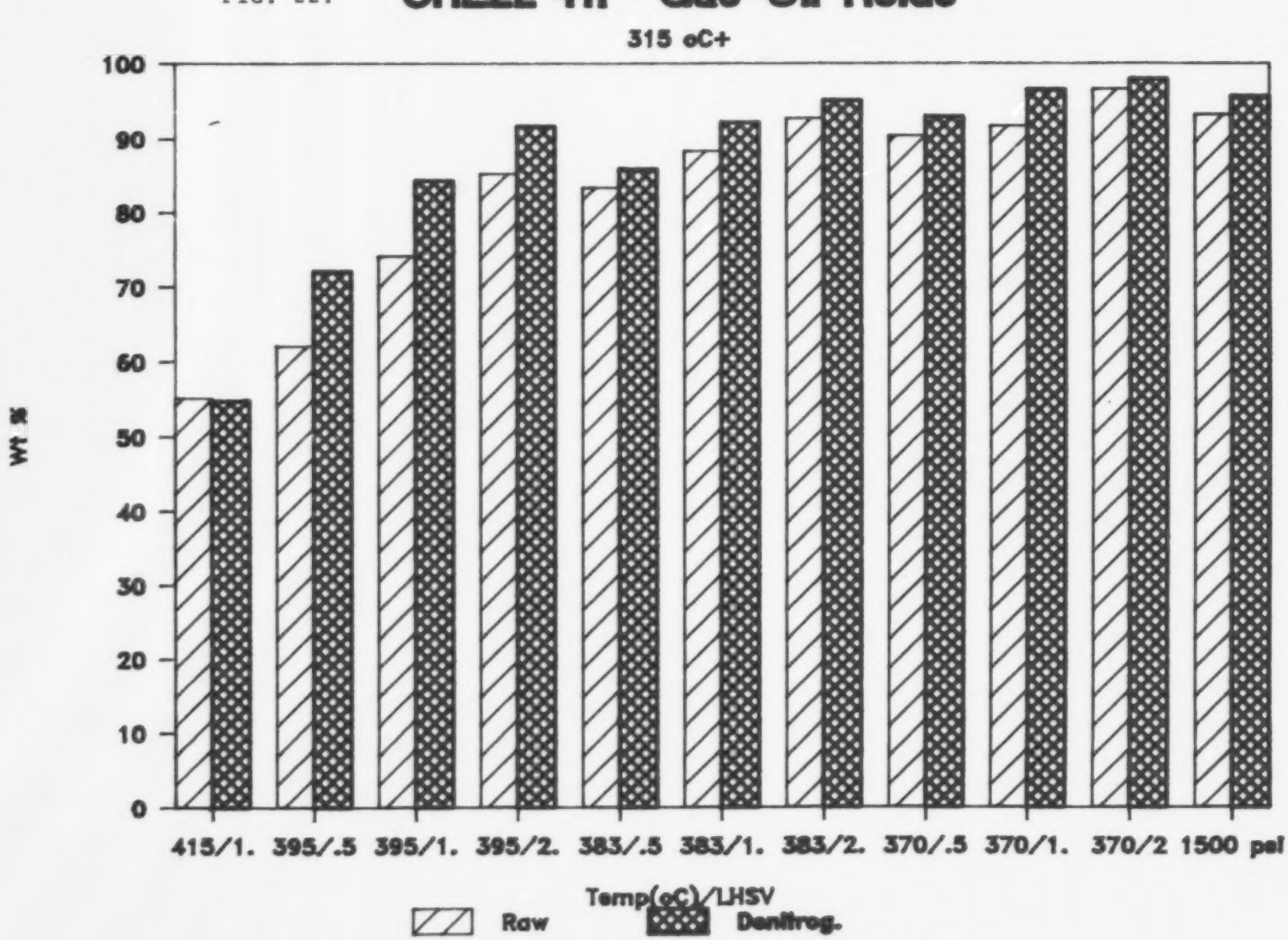

SHELL 411 - Gas-Oil Yields
315 oC+
Wt %
100
90
80
70
60
50
40
30
20
10
0
415/1.
395/.5
395/1.
395/2.
383/.5
383/1.
383/2.
370/.5
370/1.
370/2
1500 psi
Temp(oC)/LHSV
Raw
Denitrog.

FIG. 23:

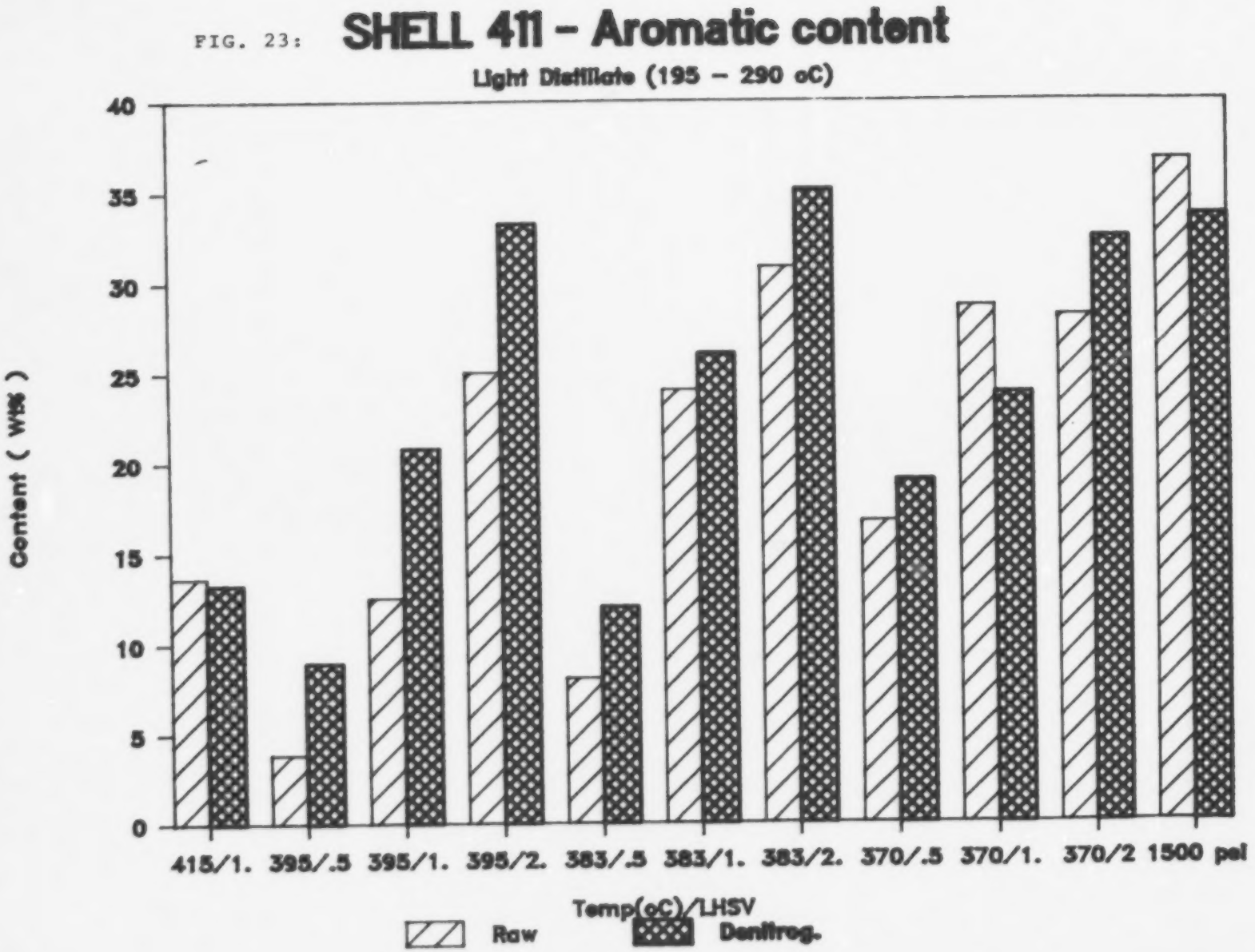

SHELL 411 - Aromatic content
Light Distillate (195 - 290 oC)
Content (Wt%)
40
35
30
25
20
15
10
5
0
415/1.
395/.5
395/1.
395/2.
383/.5
383/1.
383/2.
370/.5
370/1.
370/2
1500 psi
Temp(oC)/LHSV
Raw
Denitrog.

FIG. 24:

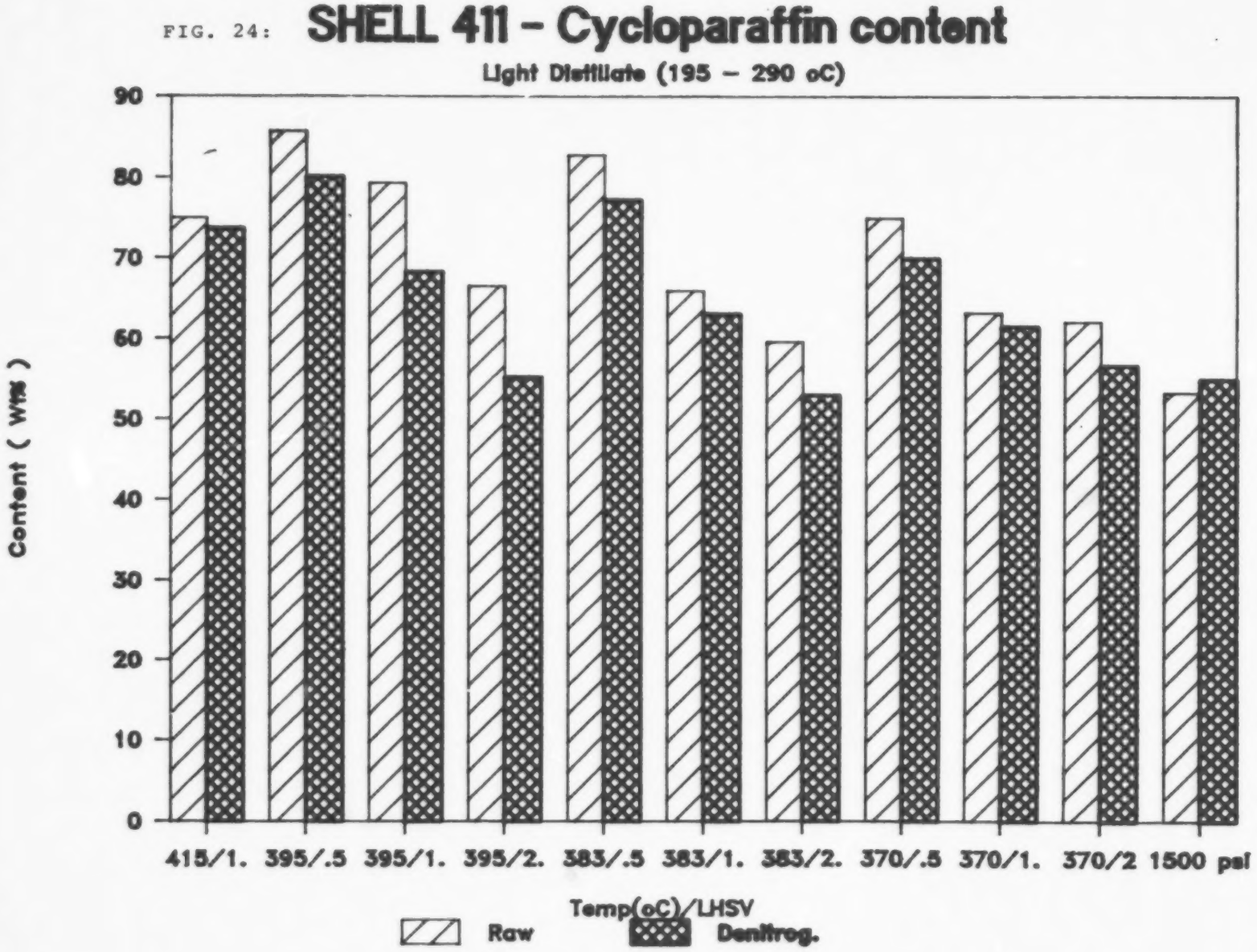

SHELL 411 - Cycloparaffin content
Light Distillate (195 - 290 oC)
Content (Wts)
90
80
70
60
50
40
30
20
10
0
415/1.
395/.5
395/1.
395/2.
383/.5
383/1.
383/2.
370/.5
370/1.
370/2
1500 psi
Temp(oC)/LHSV
Raw
Denitrog.

FIG. 25:

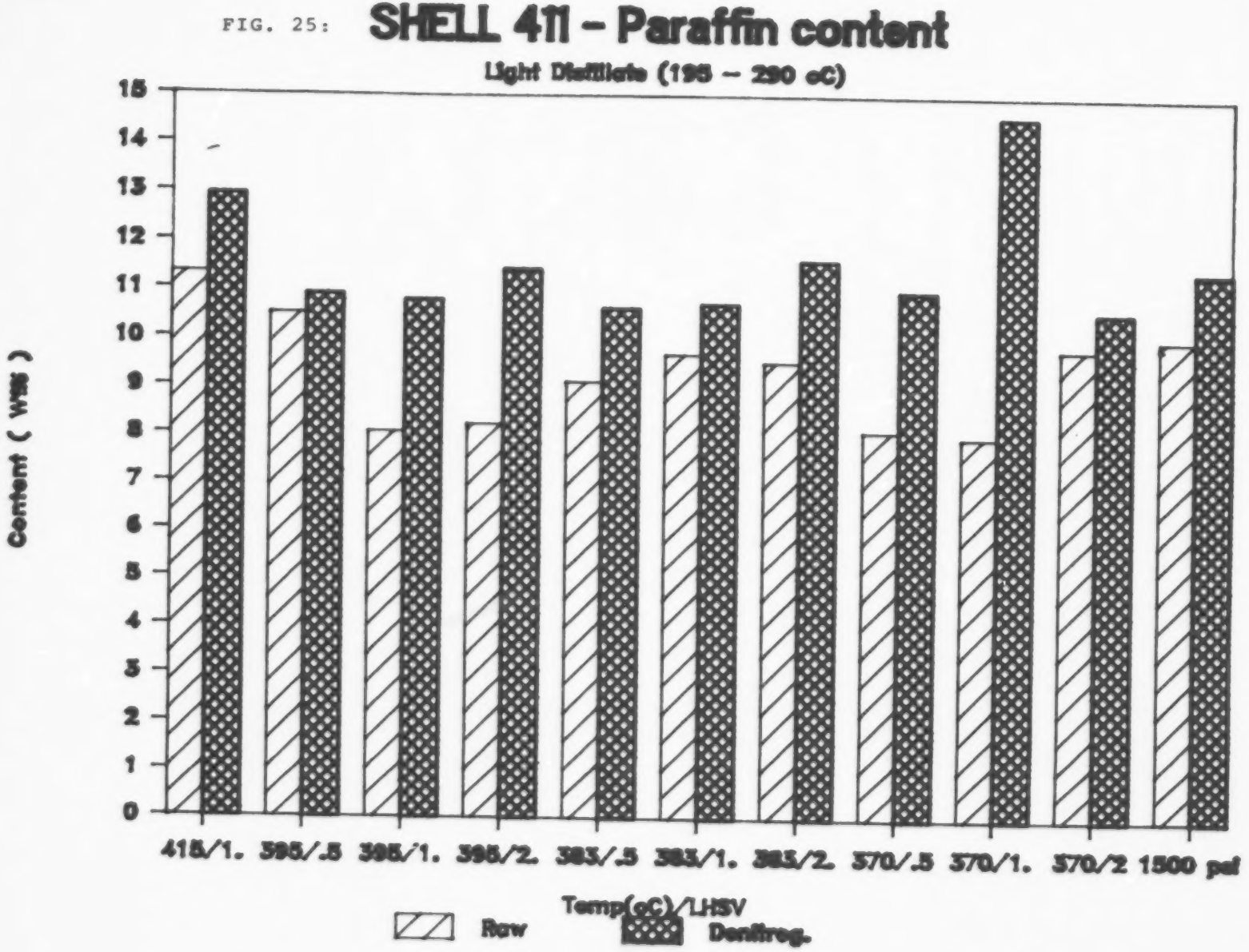

SHELL 411 - Paraffin content
Light Distillate (195 - 290 oC)
Content (Wt%)
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
415/1.
395/.5
395/1.
395/2.
383/.5
383/1.
383/2.
370/.5
370/1.
370/2
1500 psi
Temp(oC)/LHSV
Raw
Denitrog.

FIG. 26:

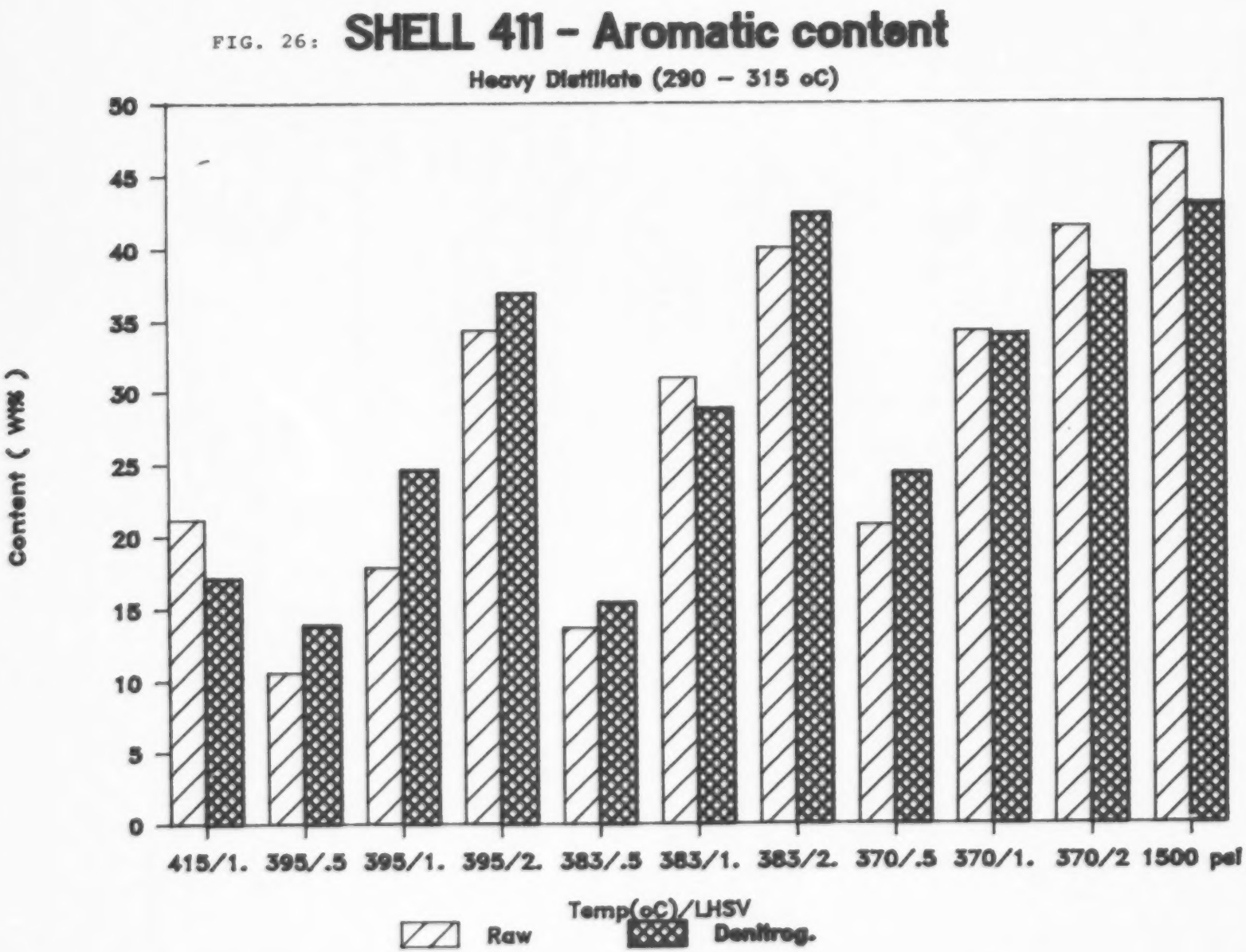

SHELL 411 - Aromatic content
Heavy Distillate (290 - 315 oC)
Content (Wt%)
50
45
40
35
30
25
20
15
10
5
0
415/1.
395/.5
395/1.
395/2.
383/.5
383/1.
383/2.
370/.5
370/1.
370/2
1500 psi
Temp(oC)/LHSV
Raw
Denitrog.

FIG. 27:

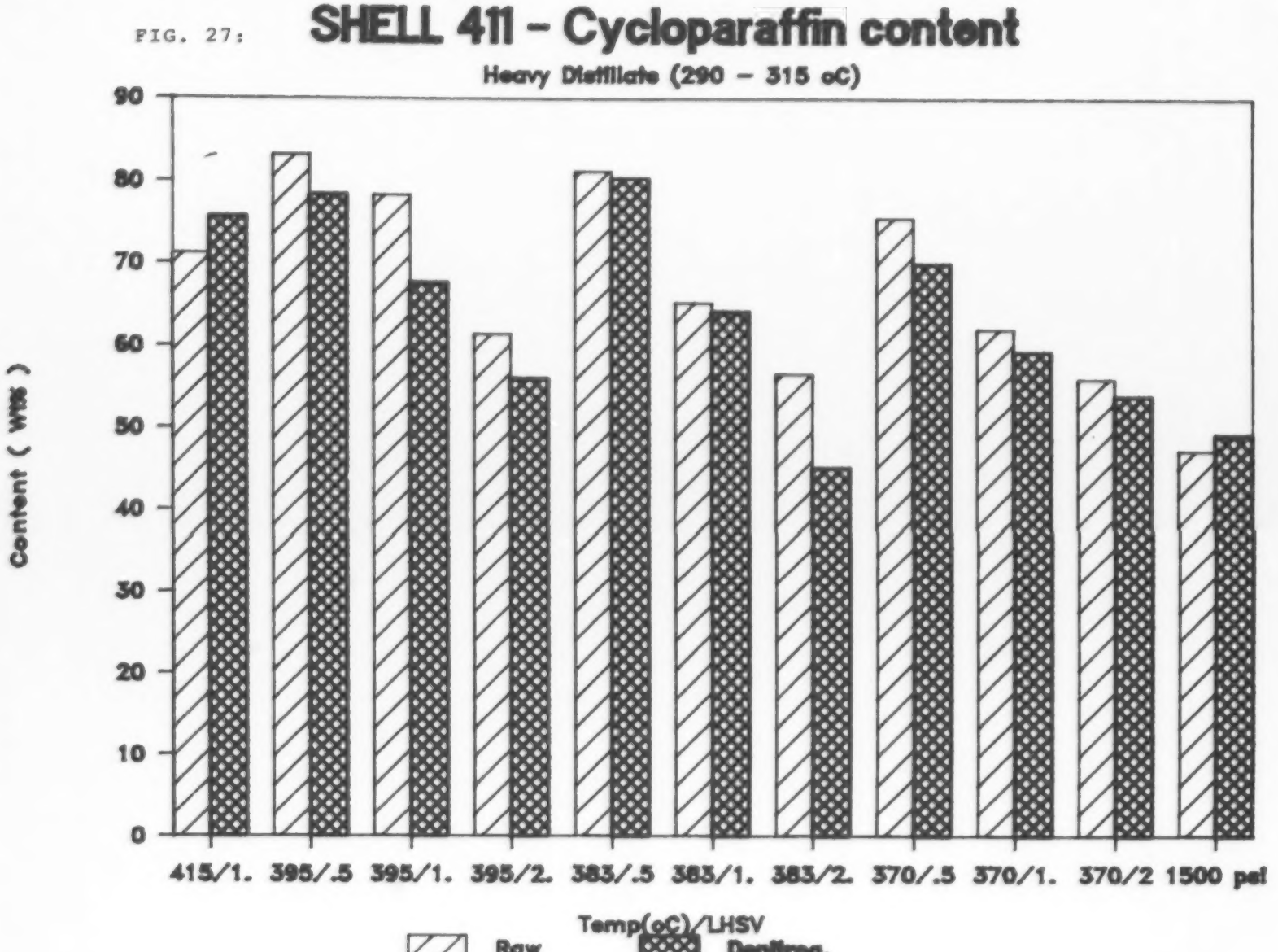

SHELL 411 - Cycloparaffin content
Heavy Distillate (290 - 315 oC)
Content (Wt%)
90
80
70
60
50
40
30
20
10
0
415/1.
395/.5
395/1.
395/2.
383/.5
383/1.
383/2.
370/.5
370/1.
370/2
1500 psi
Temp(oC)/LHSV
Raw
Denitreg.

FIG. 28:

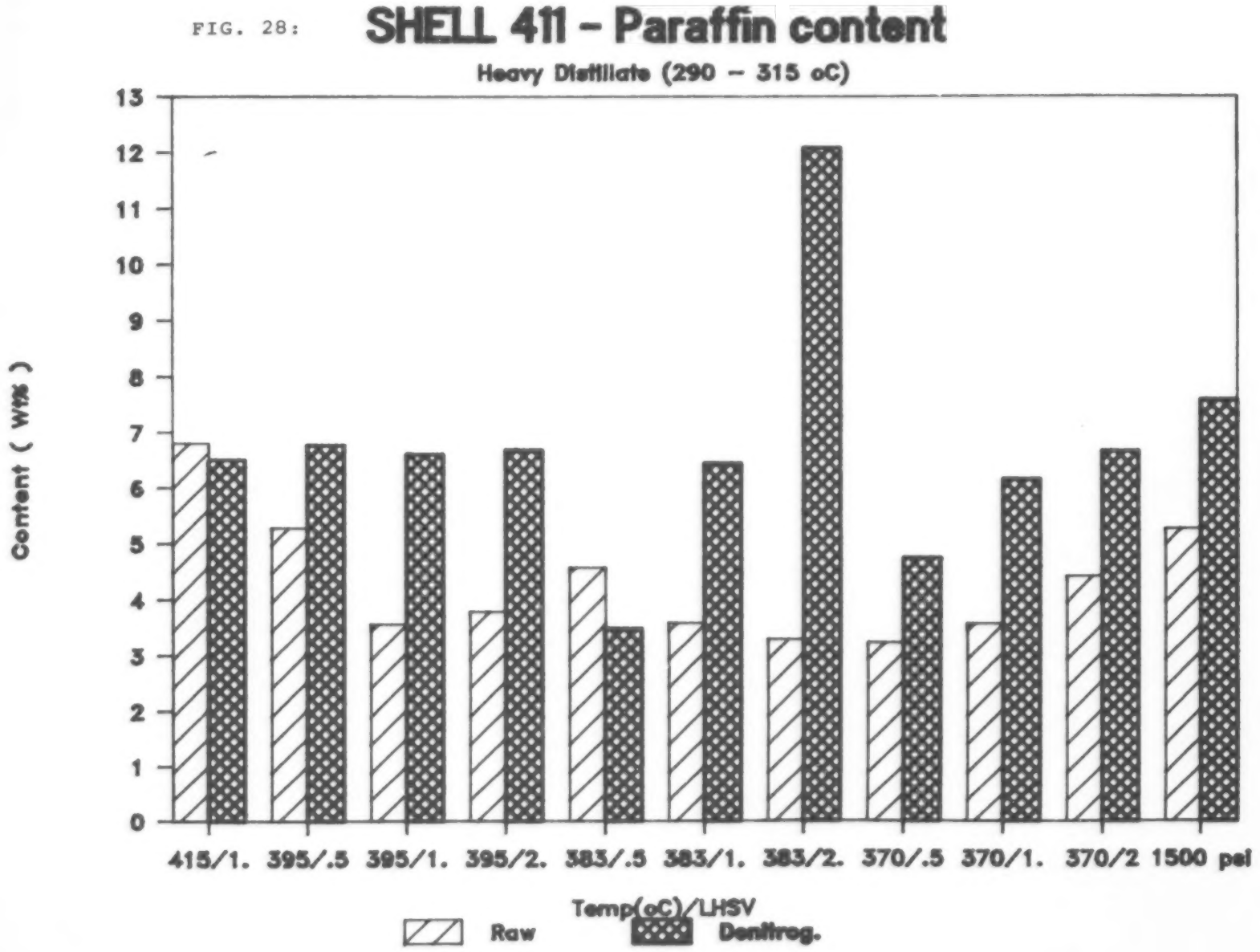

SHELL 411 - Paraffin content
Heavy Distillate (290 - 315 oC)
Content (Wt%)
13
12
11
10
9
8
7
6
5
4
3
2
1
0
415/1.
395/.5
395/1.
395/2.
383/.5
383/1.
383/2.
370/.5
370/1.
370/2
1500 psi
Temp(oC)/LHSV
Raw
Denitrog.

FIG. 29:

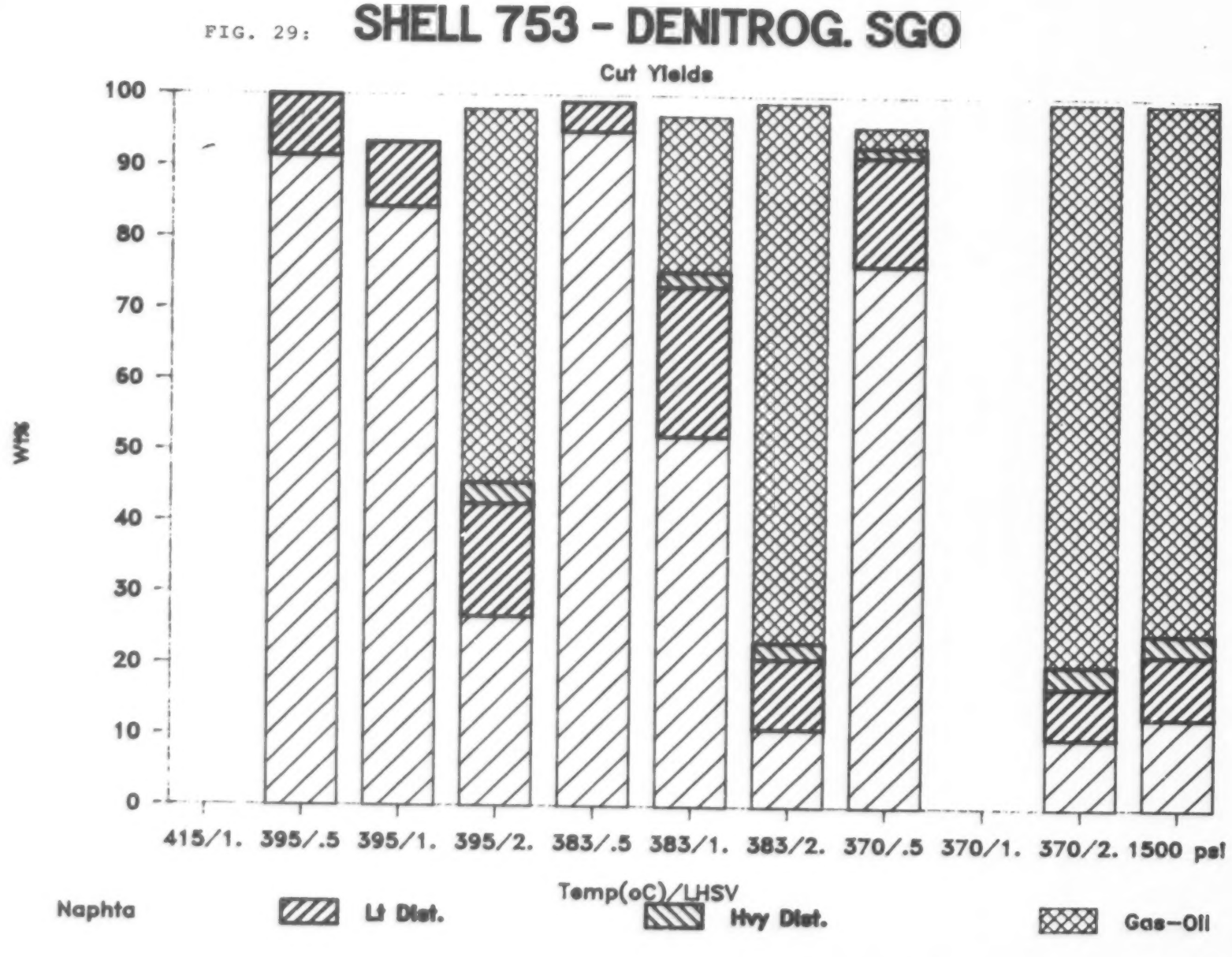

SHELL 753 - DENITROG. SGO
Cut Yields
Wt%
100
90
80
70
60
50
40
30
20
10
0
415/1.
395/.5
395/1.
395/2.
383/.5
383/1.
383/2.
370/.5
370/1.
370/2.
1500 psi
Temp(oC)/LHSV
Naphta
Lt Dist.
Hvy Dist.
Gas-Oil

FIG. 30:

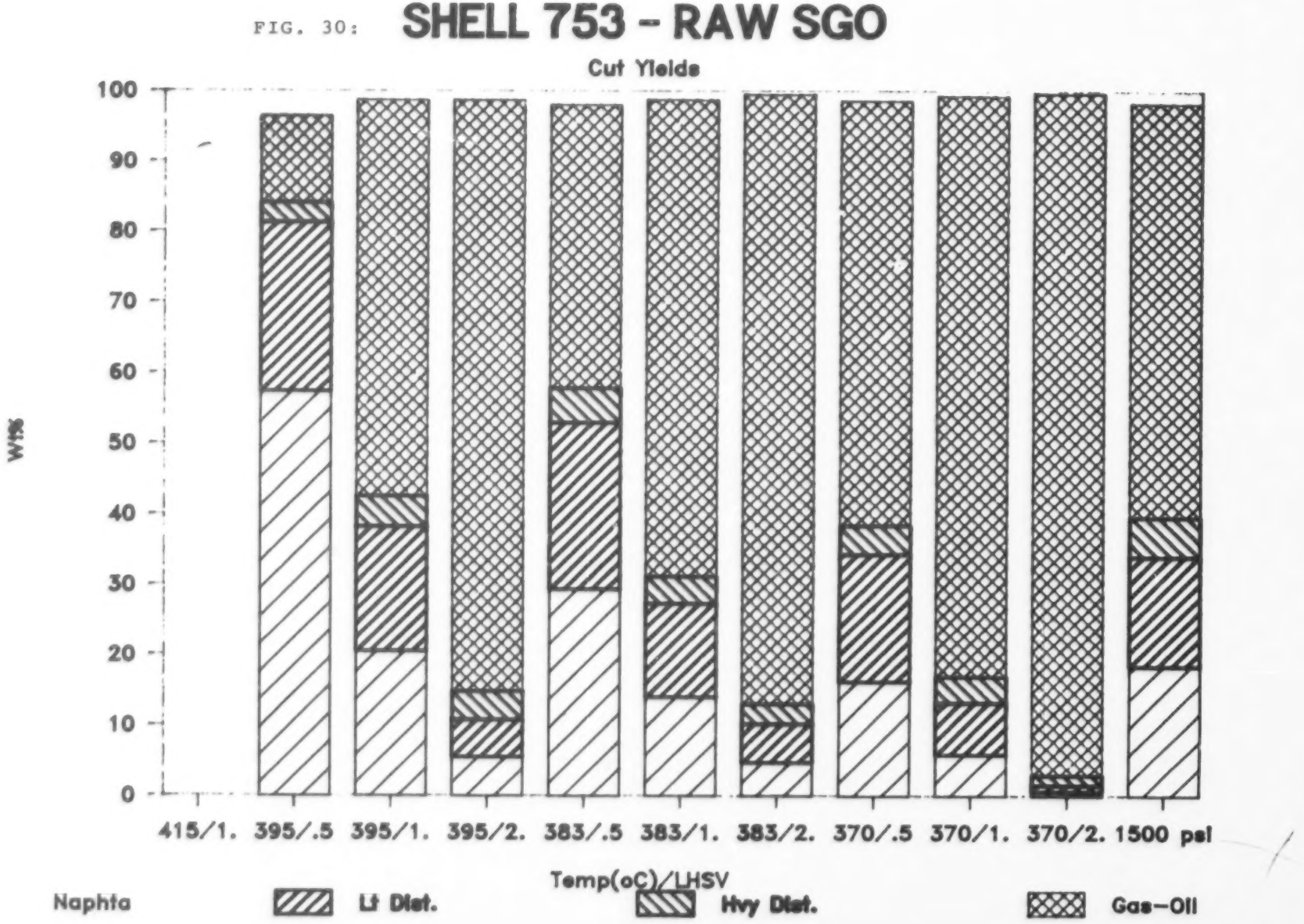

SHELL 753 - RAW SGO
Cut Yields
Wt%
100
90
80
70
60
50
40
30
20
10
0
415/1.
395/.5
395/1.
395/2.
383/.5
383/1.
383/2.
370/.5
370/1.
370/2.
1500 psi
Temp(oC)/LHSV
Naphta
Lt Dist.
Hvy Dist.
Gas-Oil

FIG. 31:

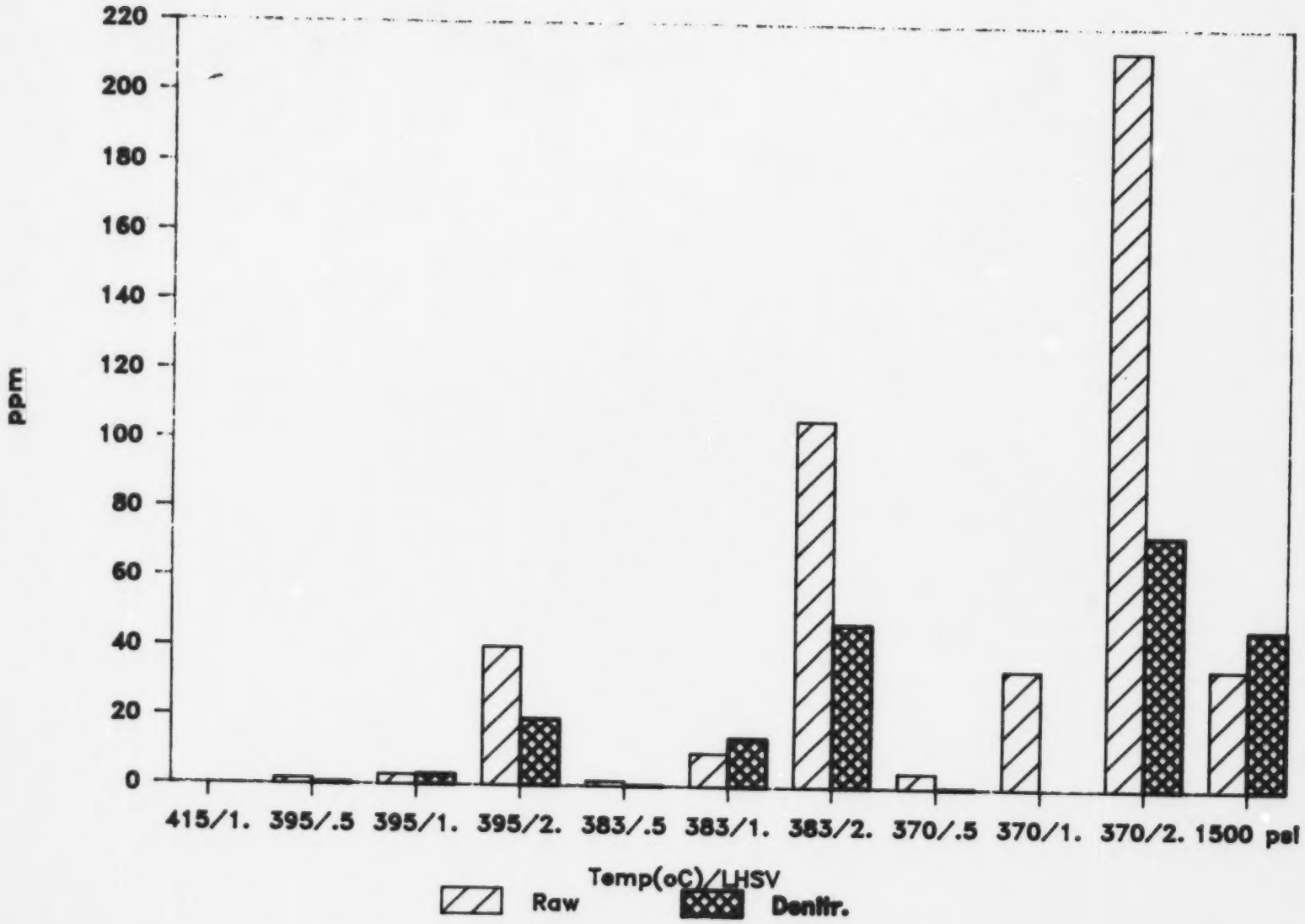

SHELL 753 - Nitrogen in TLP
ppm
220
200
180
160
140
120
100
80
60
40
20
0
415/1.
395/.5
395/1.
395/2.
383/.5
383/1.
383/2.
370/.5
370/1.
370/2.
1500 psi
Temp(oC)/LHSV
Raw
Denitr.

FIG. 32: **SHELL 753 - Naphtha Yields**

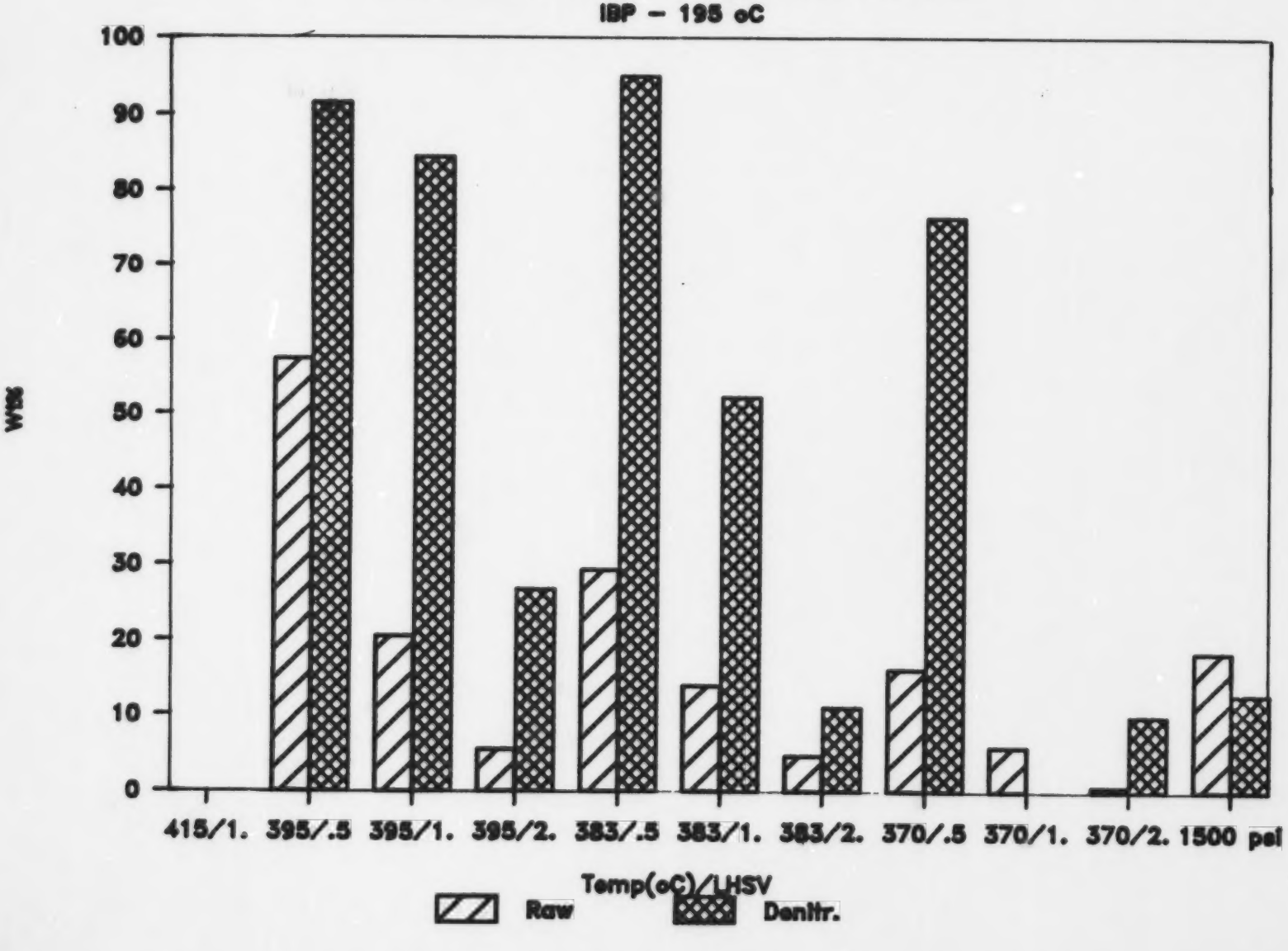


FIG. 33: **SHELL 753 - Light Distillate Yields**

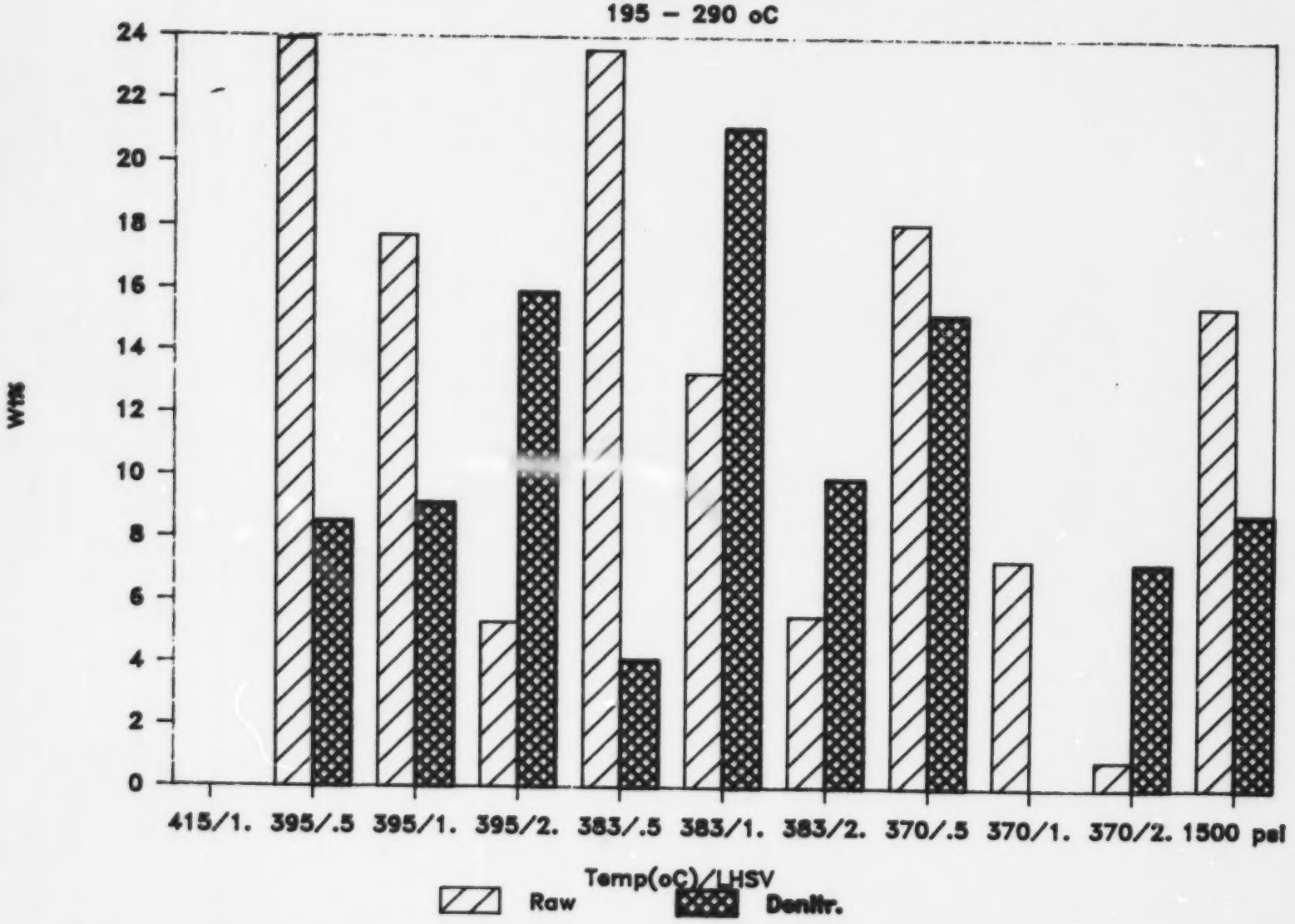


FIG. 34: **SHELL 753 - Heavy Distillate Yields**

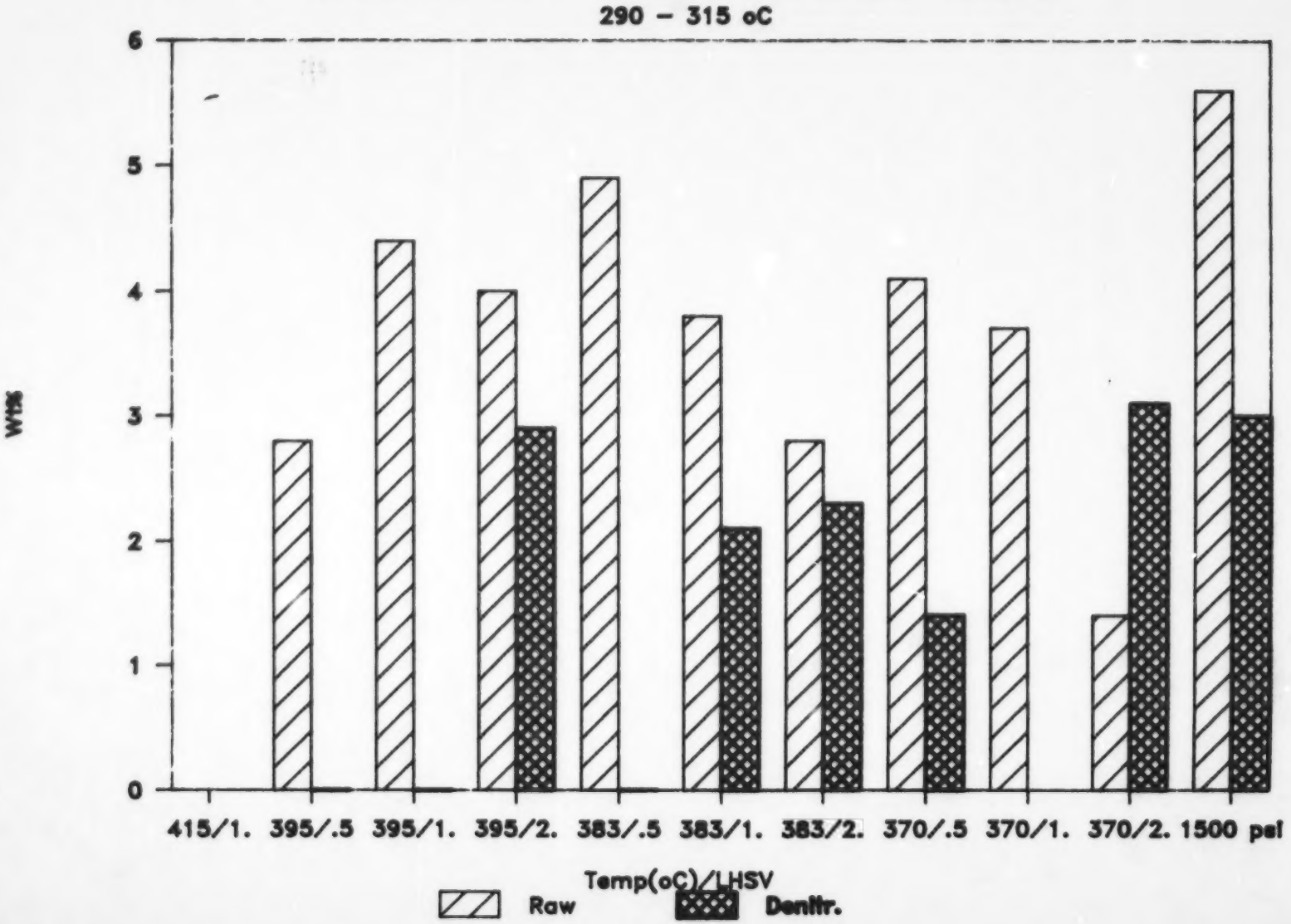


FIG. 35:

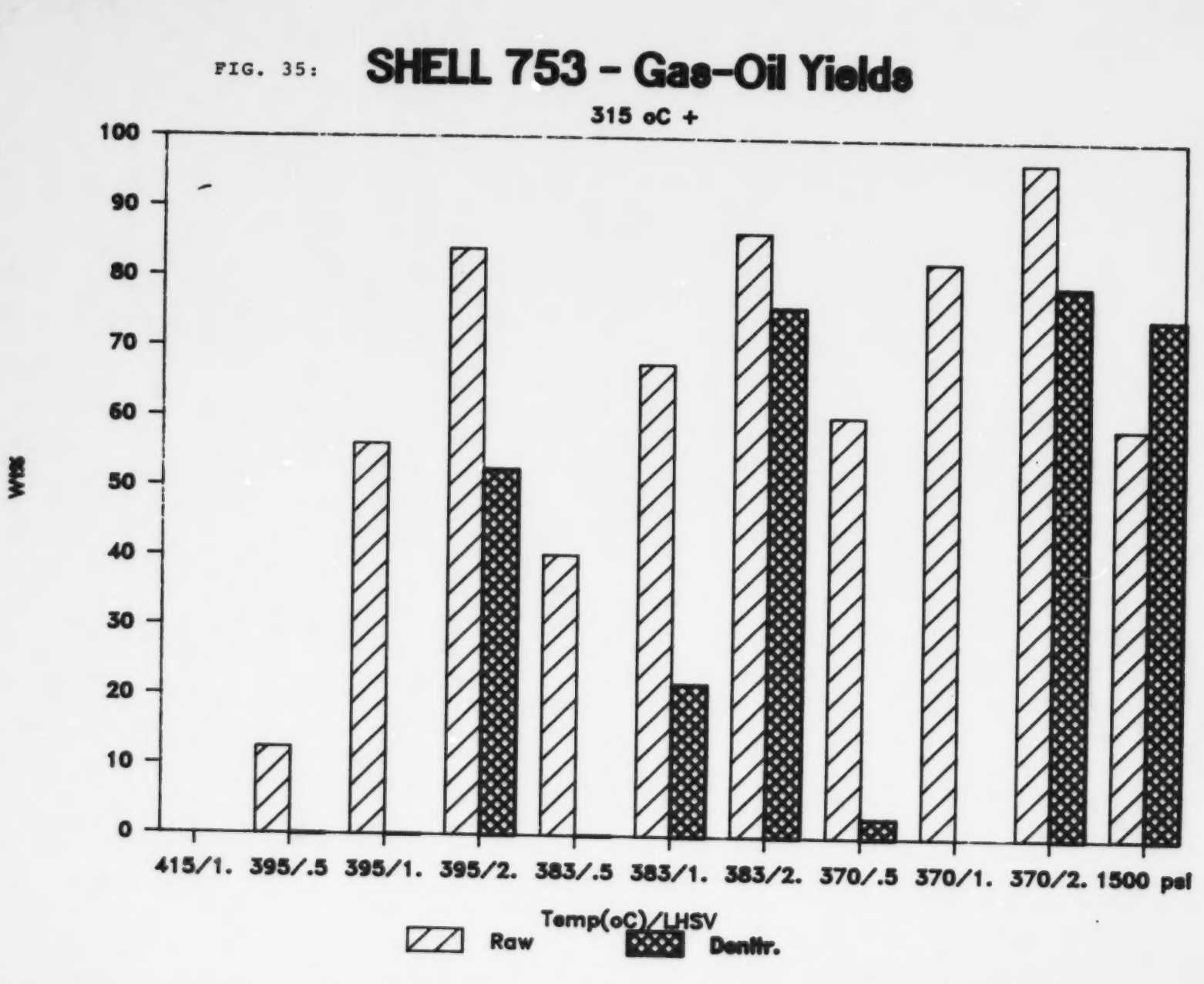

SHELL 753 - Gas-Oil Yields
315 oC +
Wts
100
90
80
70
60
50
40
30
20
10
0
415/1.
395/.5
395/1.
395/2.
383/.5
383/1.
383/2.
370/.5
370/1.
370/2.
1500 psi
Temp(oC)/LHSV
Raw
Denitr.

FIG. 36:

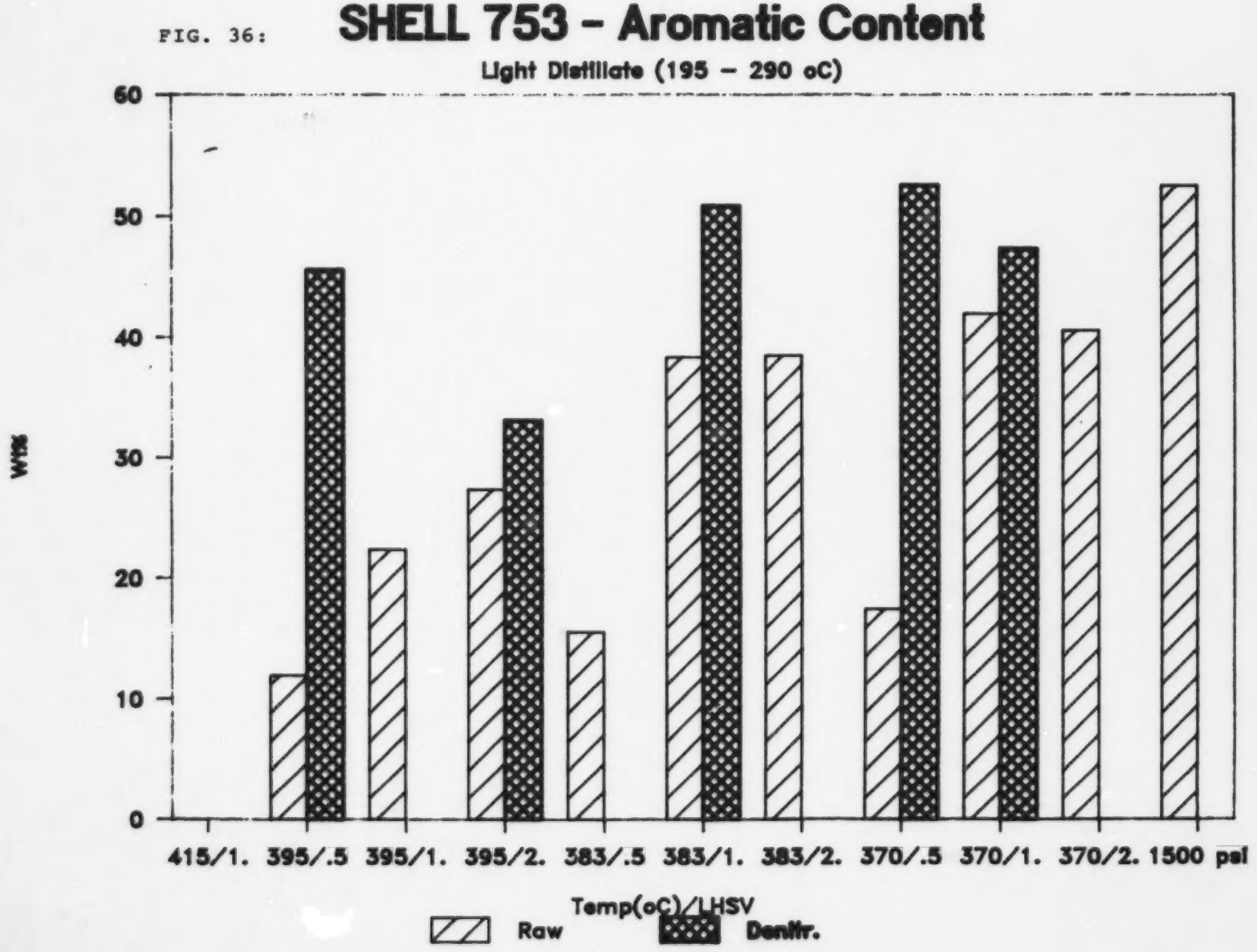

SHELL 753 - Aromatic Content
Light Distillate (195 - 290 oC)
60
50
40
30
20
10
0
Wt%
415/1.
395/.5
395/1.
395/2.
383/.5
383/1.
383/2.
370/.5
370/1.
370/2.
1500 psi
Temp(oC)/LHSV
Raw
Denitr.

FIG. 37: **SHELL 753 - Cycloparaffin Content**

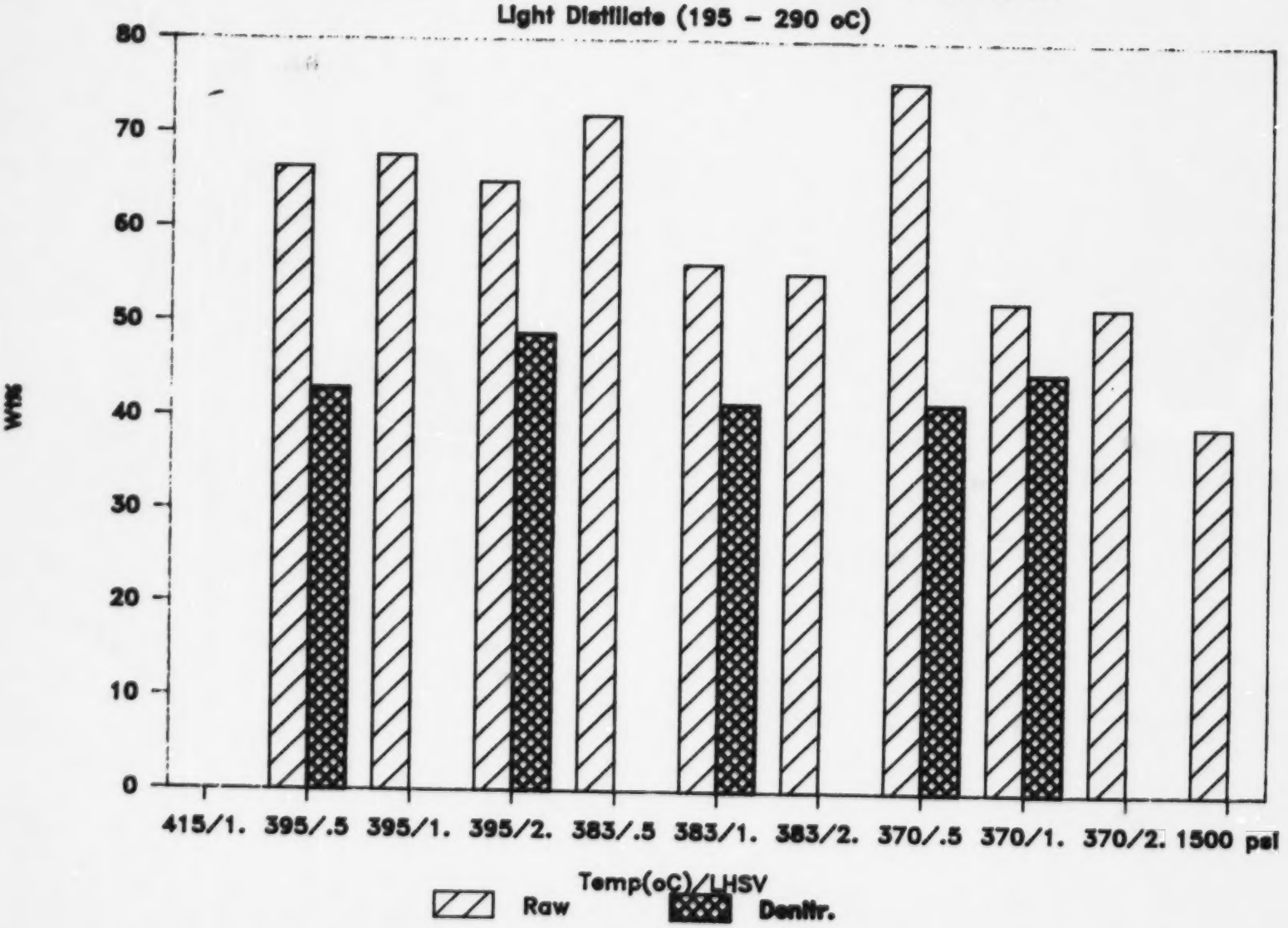


FIG. 38:

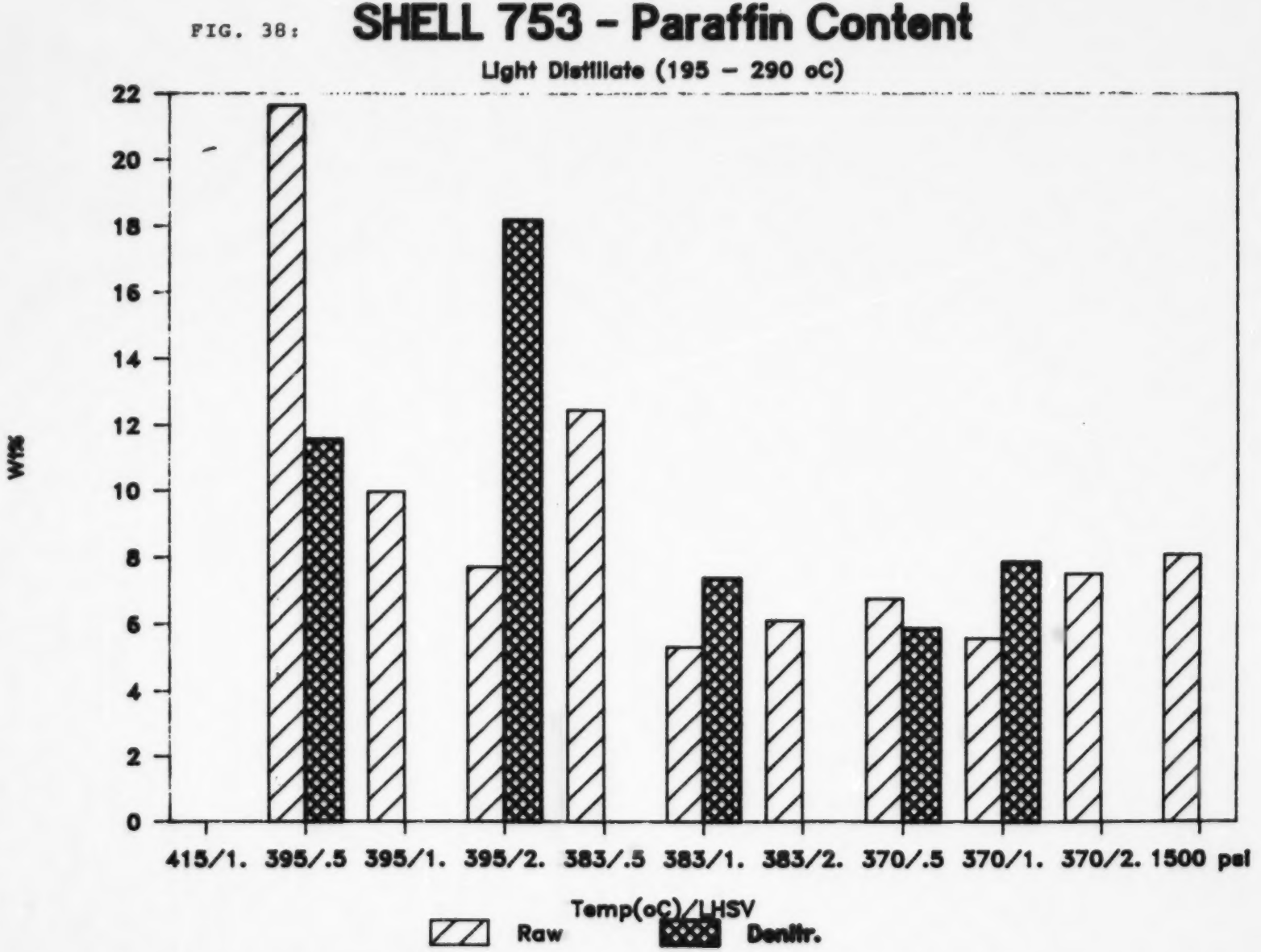

SHELL 753 - Paraffin Content
Light Distillate (195 - 290 oC)
wt%
22
20
18
16
14
12
10
8
6
4
2
0
415/1.
395/.5
395/1.
395/2.
383/.5
383/1.
383/2.
370/.5
370/1.
370/2.
1500 psi
Temp(oC)/LHSV
Raw
Denitr.

FIG. 39:

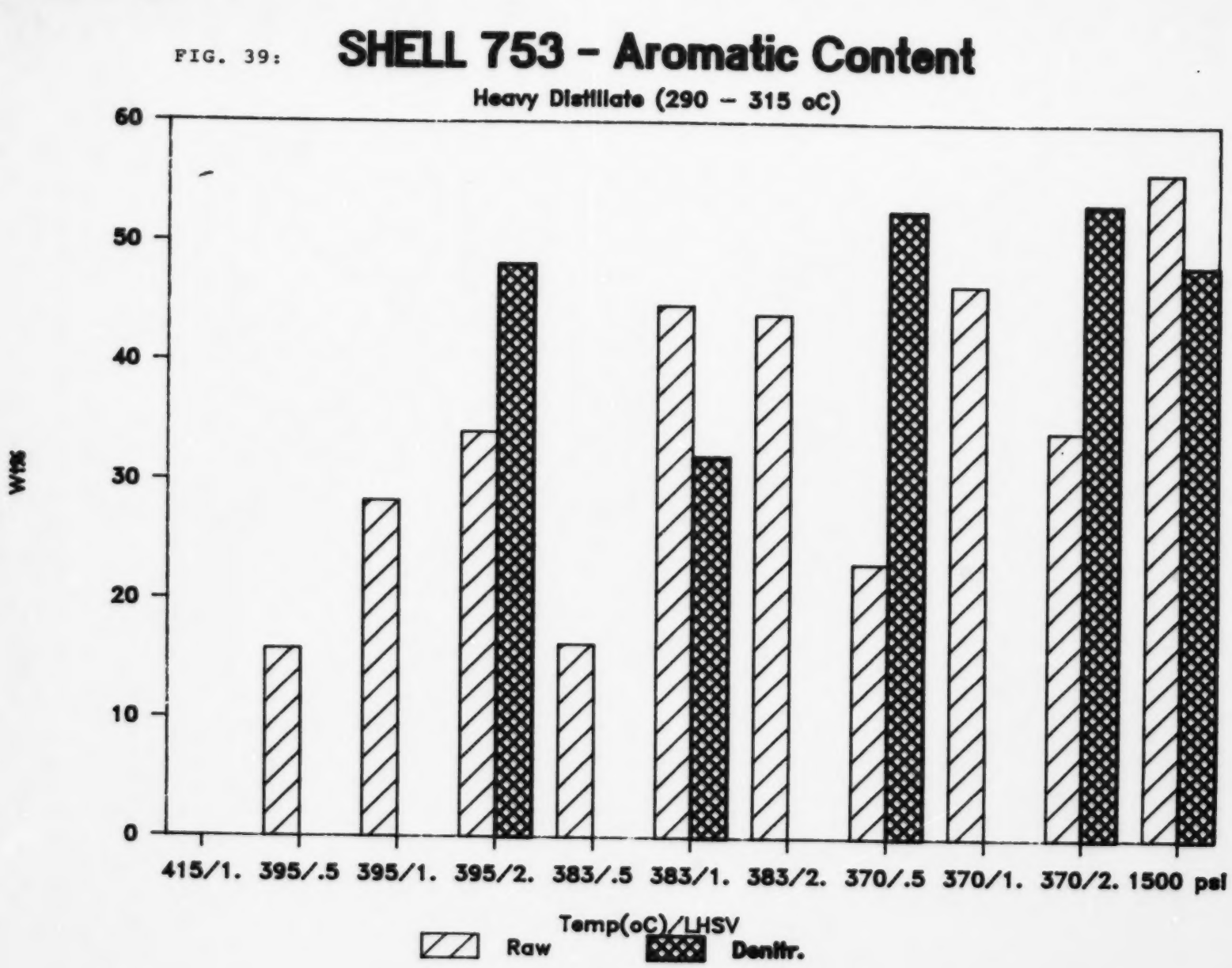

SHELL 753 - Aromatic Content
Heavy Distillate (290 – 315 oC)
60
50
40
30
20
10
0
Wt%
415/1.
395/.5
395/1.
395/2.
383/.5
383/1.
383/2.
370/.5
370/1.
370/2.
1500 psi
Temp(oC)/LHSV
Raw
Denitr.

FIG. 40:

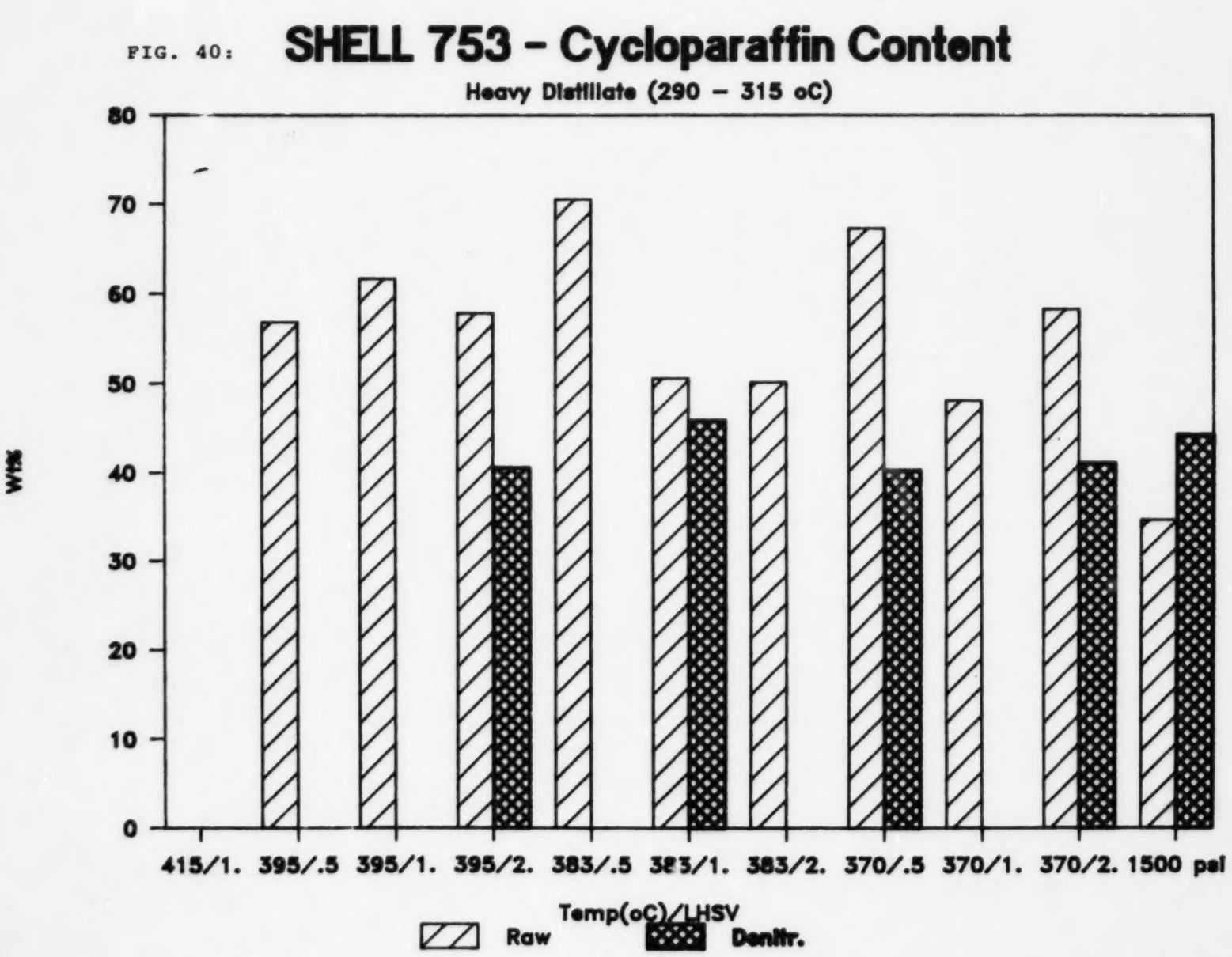

SHELL 753 - Cycloparaffin Content
Heavy Distillate (290 - 315 oC)
Wt%
80
70
60
50
40
30
20
10
0
415/1.
395/.5
395/1.
395/2.
383/.5
383/1.
383/2.
370/.5
370/1.
370/2.
1500 psi
Temp(oC)/LHSV
Raw
Denitr.

FIG. 41:

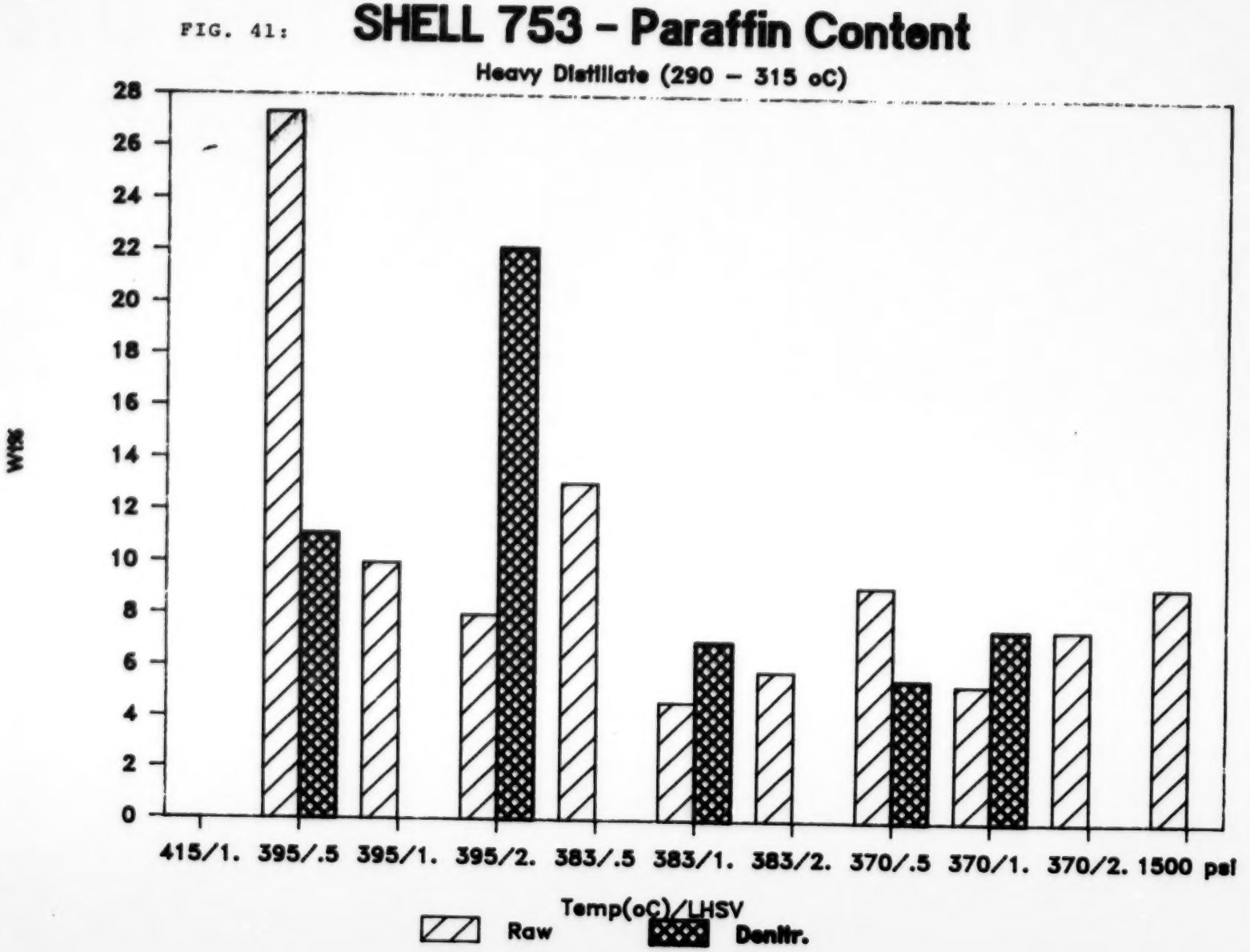

SHELL 753 - Paraffin Content
Heavy Distillate (290 – 315 oC)
WT%
28
26
24
22
20
18
16
14
12
10
8
6
4
2
0
415/1.
395/.5
395/1.
395/2.
383/.5
383/1.
383/2.
370/.5
370/1.
370/2.
1500 psi
Temp(oC)/LHSV
Raw
Denitr.

FIG. 42:

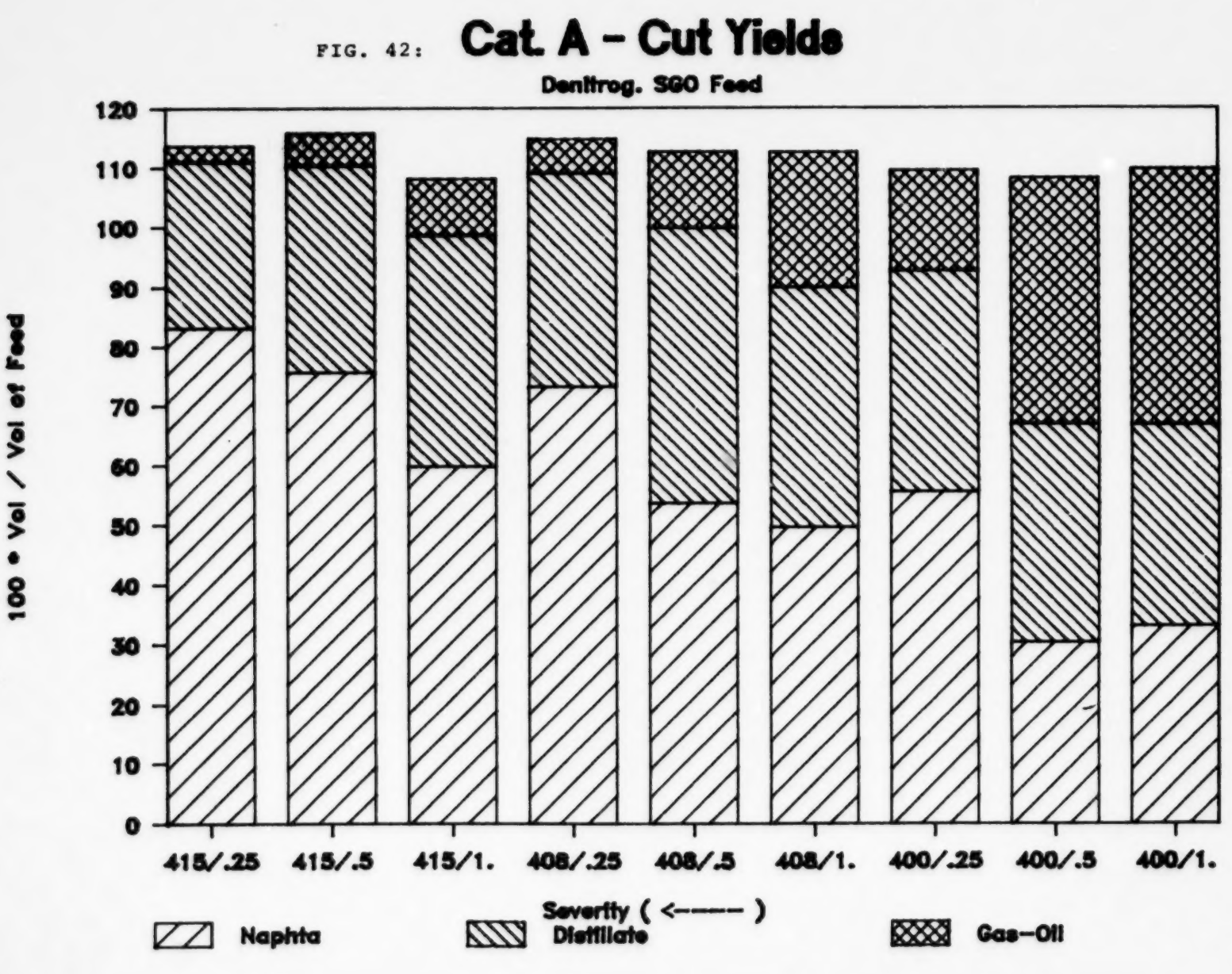

Cat. A - Cut Yields
Denitrog. SGO Feed
100 • Vol / Vol of Feed
120
110
100
90
80
70
60
50
40
30
20
10
0
415/.25
415/.5
415/1.
408/.25
408/.5
408/1.
400/.25
400/.5
400/1.
Severity (<-----)
Naphta
Distillate
Gas-Oil

FIG. 43:

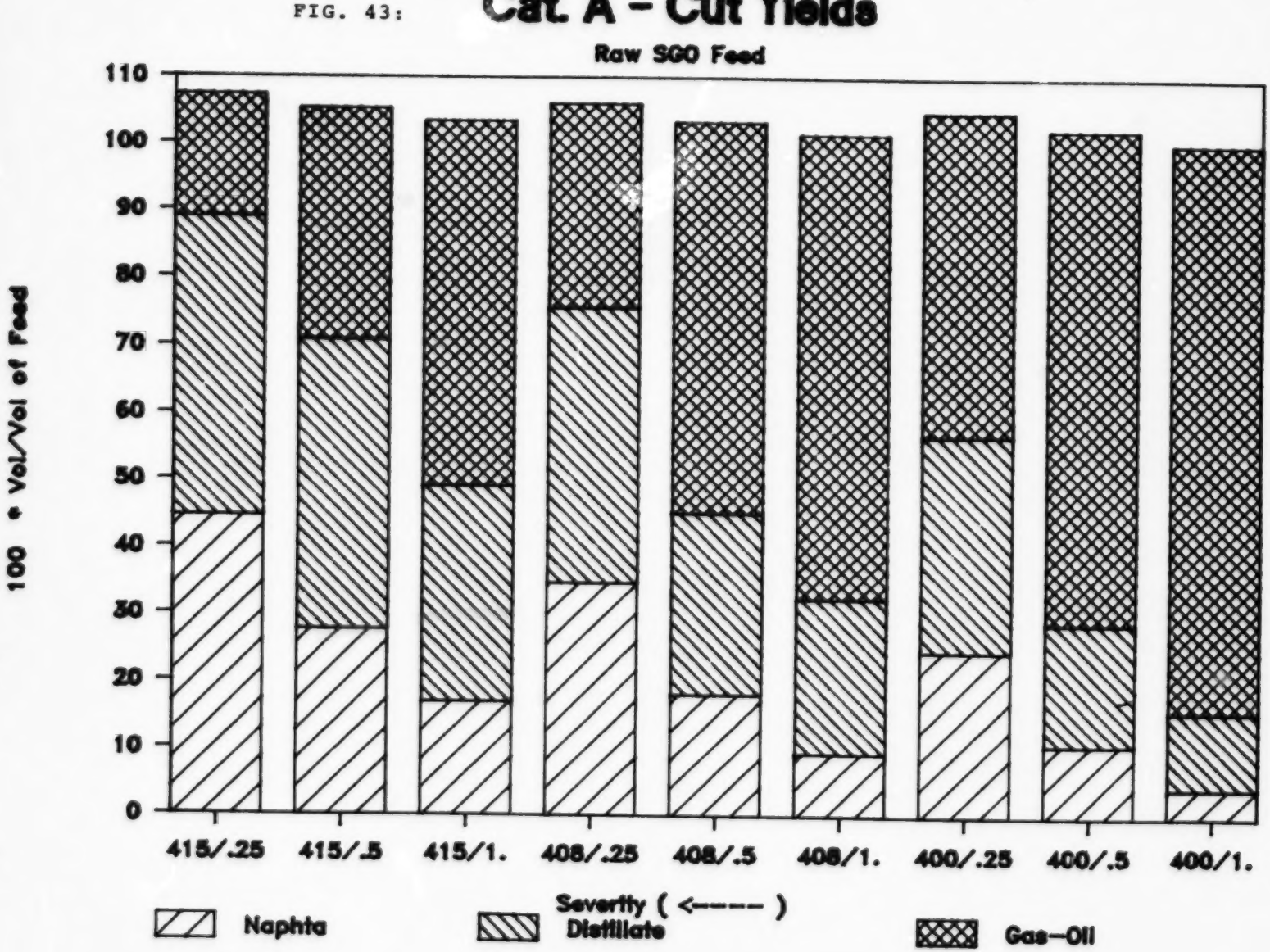

Cat. A - Cut Yields
Raw SGO Feed
100 * Vol/Vol of Feed
110
100
90
80
70
60
50
40
30
20
10
0
415/.25
415/.5
415/1.
408/.25
408/.5
408/1.
400/.25
400/.5
400/1.
Severity (<-----)
Naphta
Distillate
Gas-Oil

FIG. 44: **Cat. A - Naphtha**

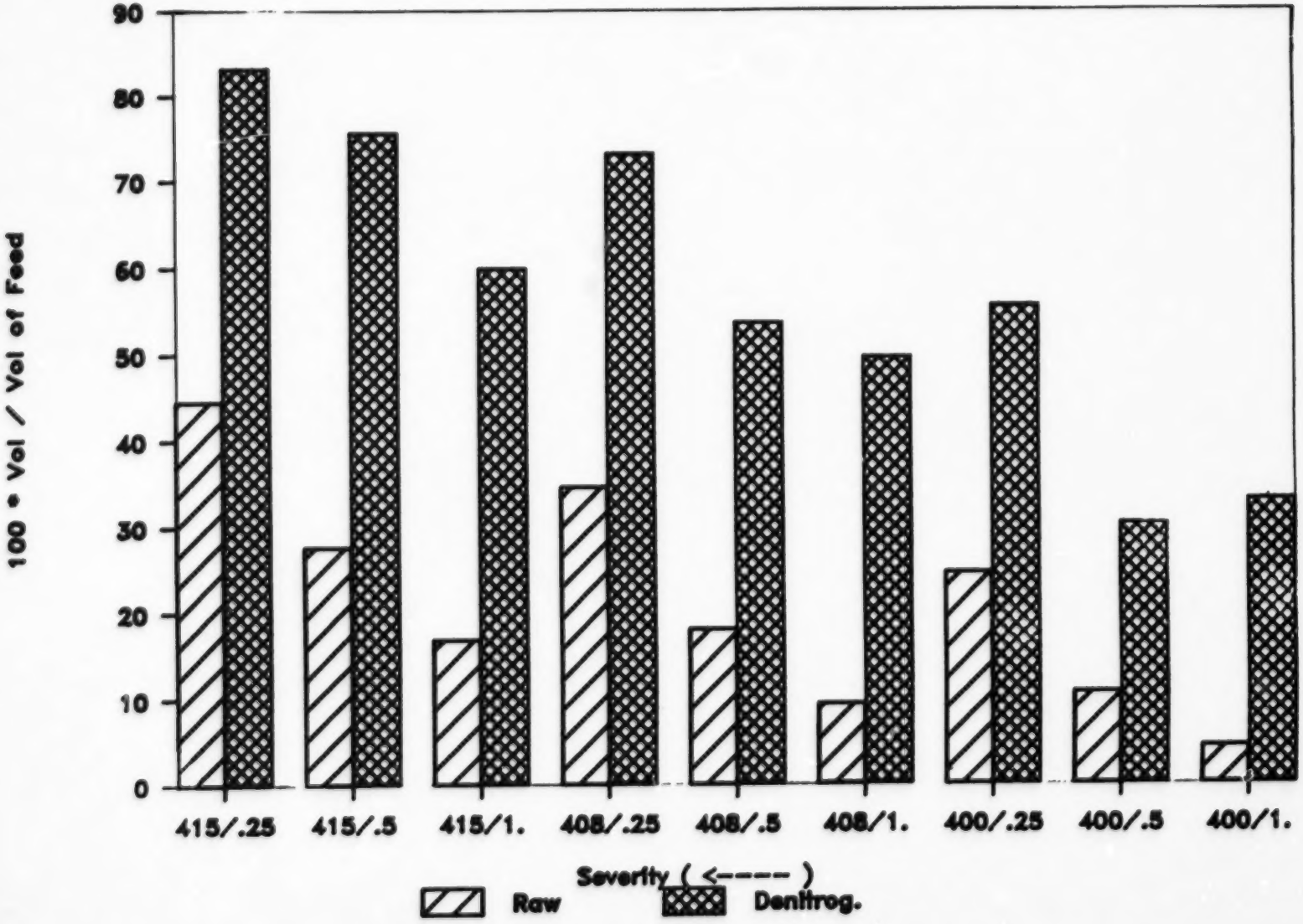


FIG. 45:

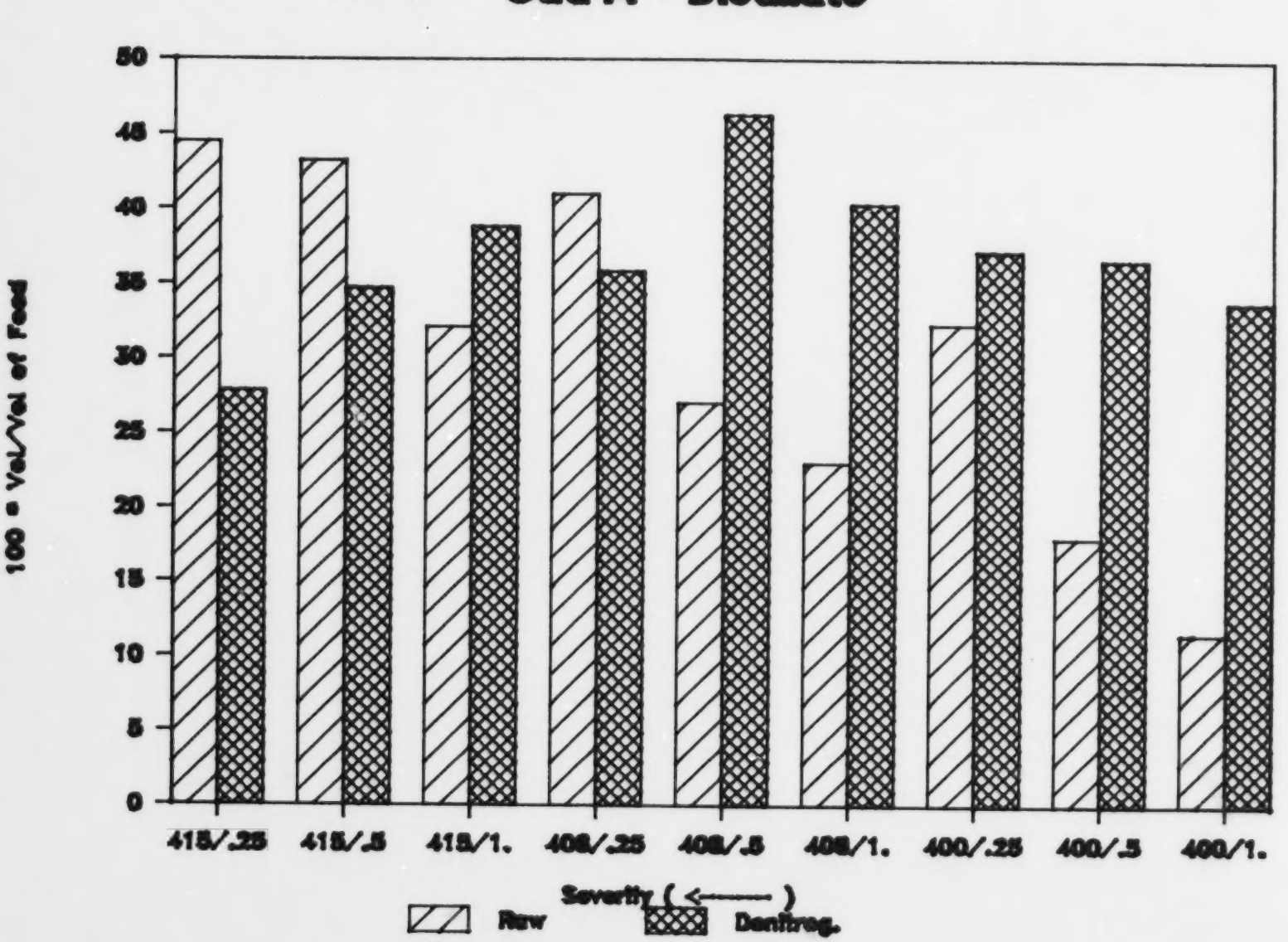

Cat. A - Distillate
100 * Vol/Vol of Feed
50
45
40
35
30
25
20
15
10
5
0
415/.25
415/.5
415/1.
408/.25
408/.5
408/1.
400/.25
400/.5
400/1.
Severity (<——)
Raw
Dentreg.

FIG. 46: **Cat. A - Gas-Oil**

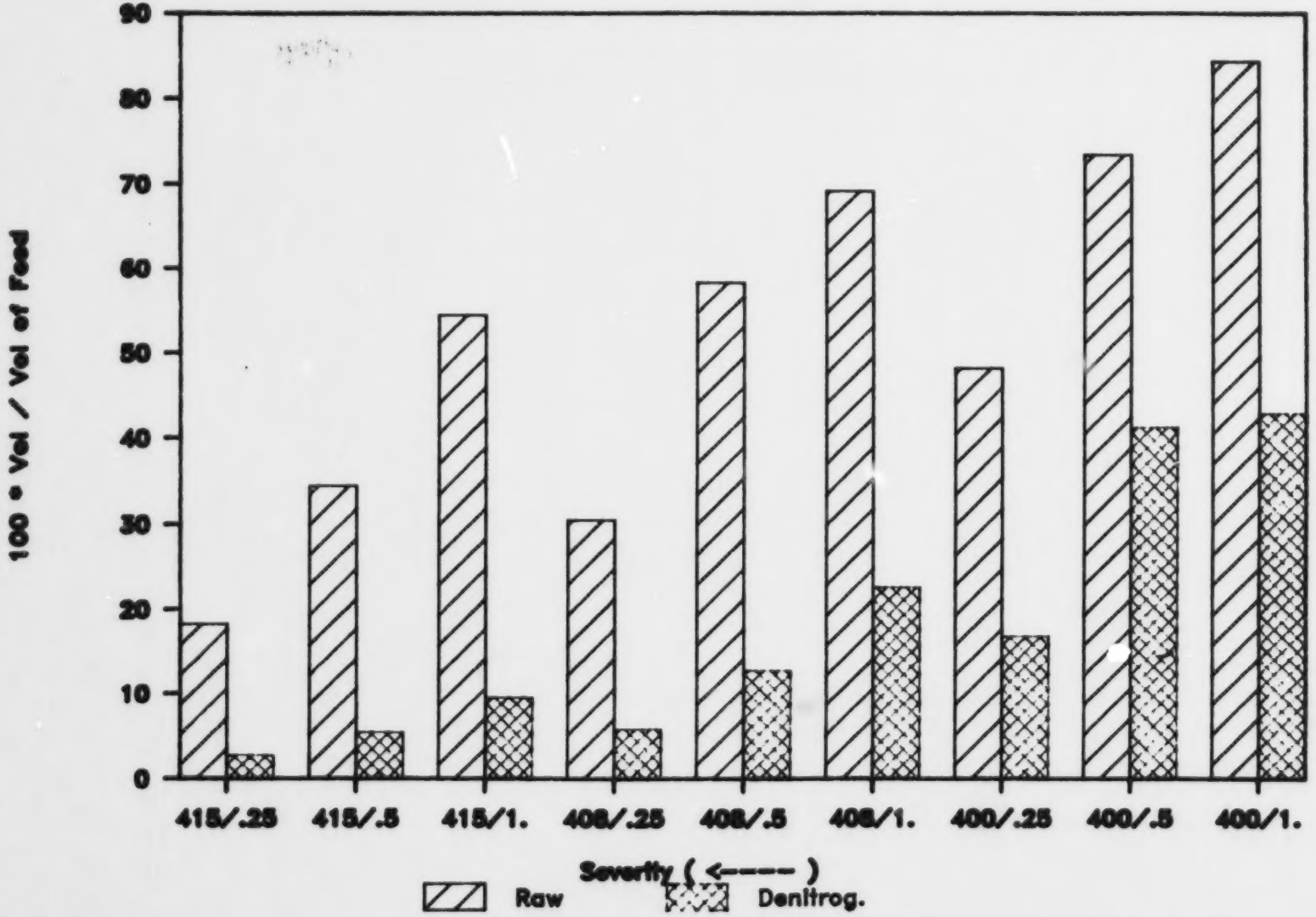


FIG.47:

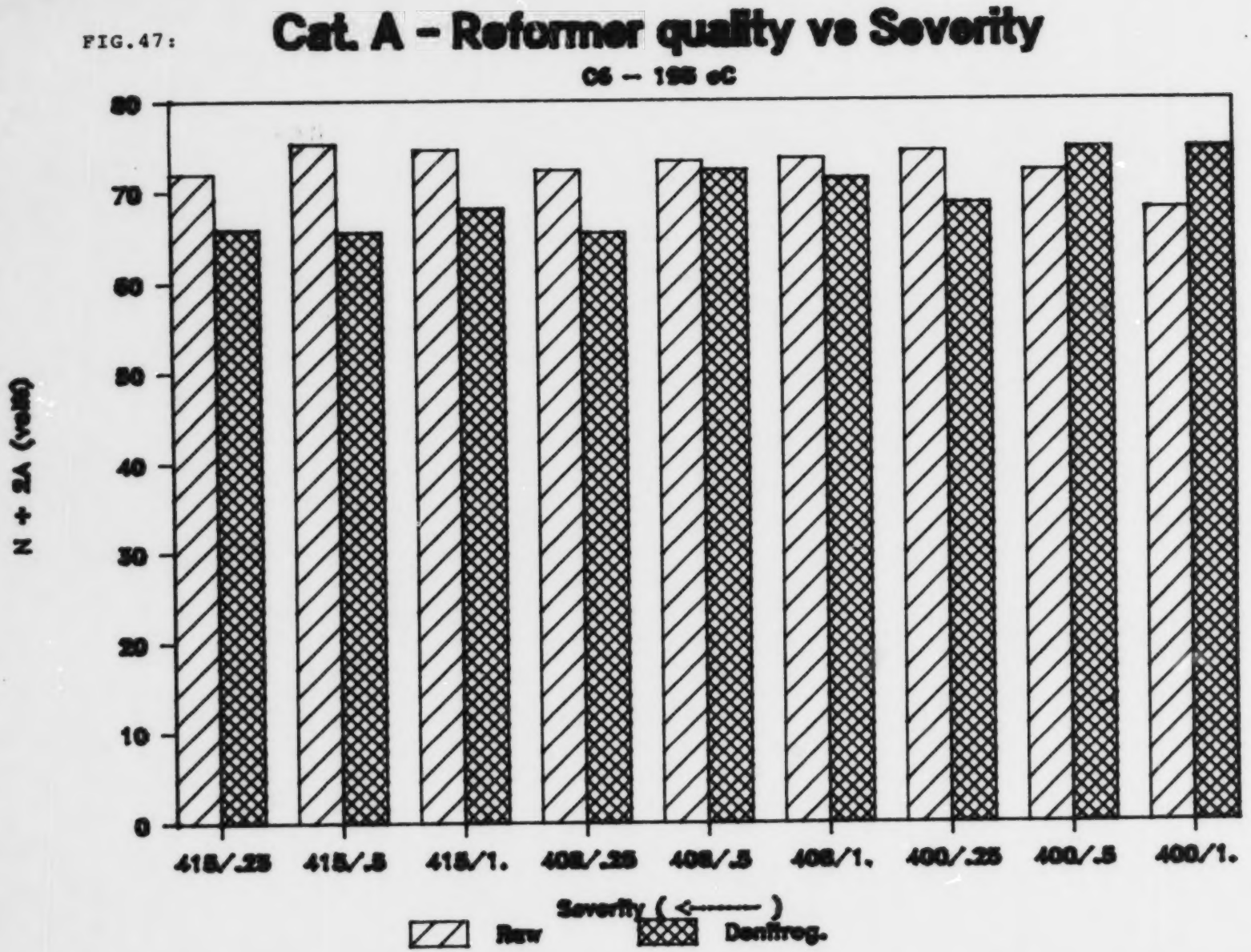

Cat. A - Reformer quality vs Severity
C6 - 195 oC
80
70
60
50
40
30
20
10
0
N + 2A (psig)
415/.25
415/.5
415/1.
408/.25
408/.5
408/1.
400/.25
400/.5
400/1.
Severity (<-------)
Raw
Denitreg.

FIG. 48:

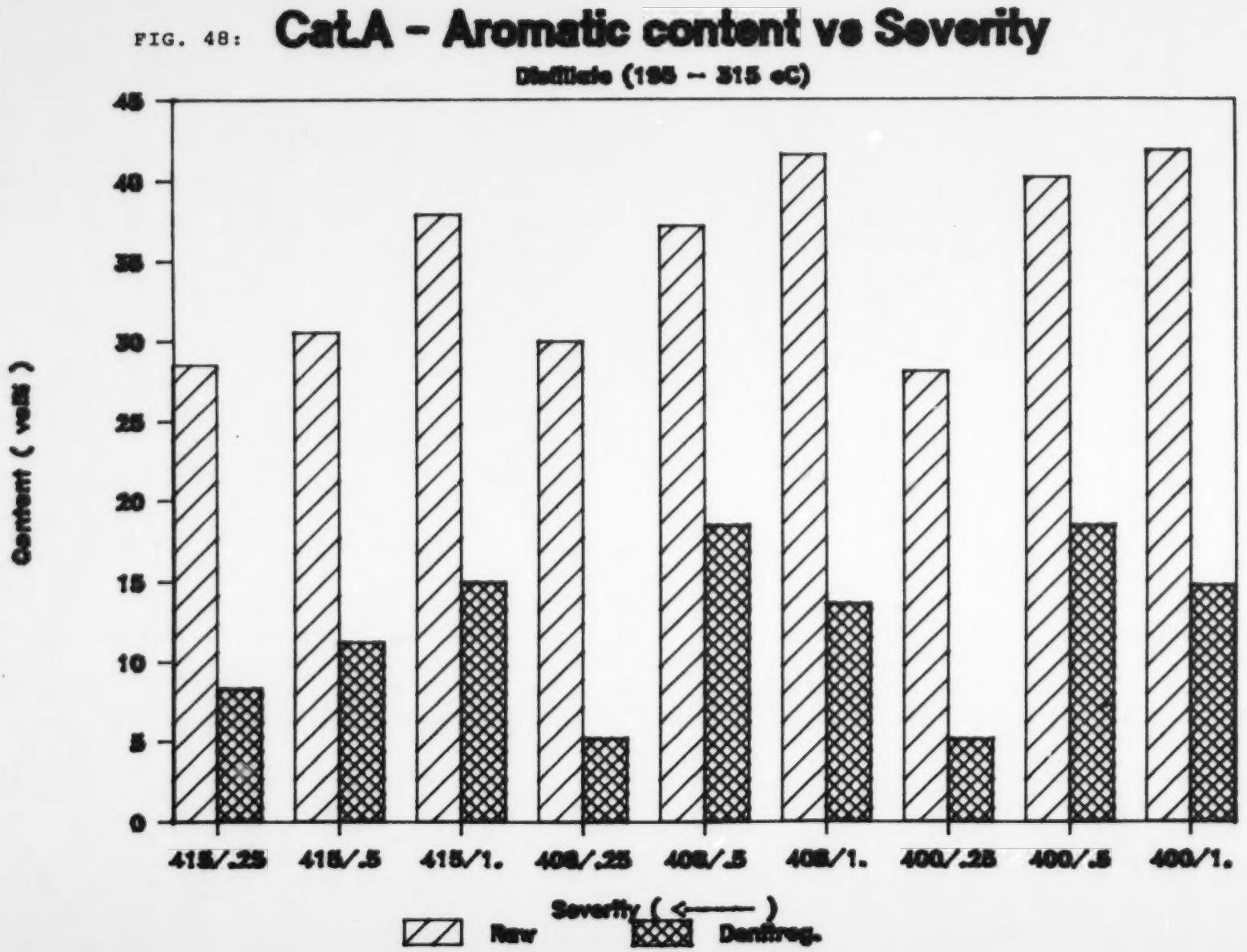

Cat.A - Aromatic content vs Severity
Distillate (195 -- 315 oC)
Content (vol%)
45
40
35
30
25
20
15
10
5
0
415/.25
415/.5
415/1.
400/.25
400/.5
400/1.
400/.25
400/.5
400/1.
Severity (<———)
Raw
Dentreg.

FIG. 49:

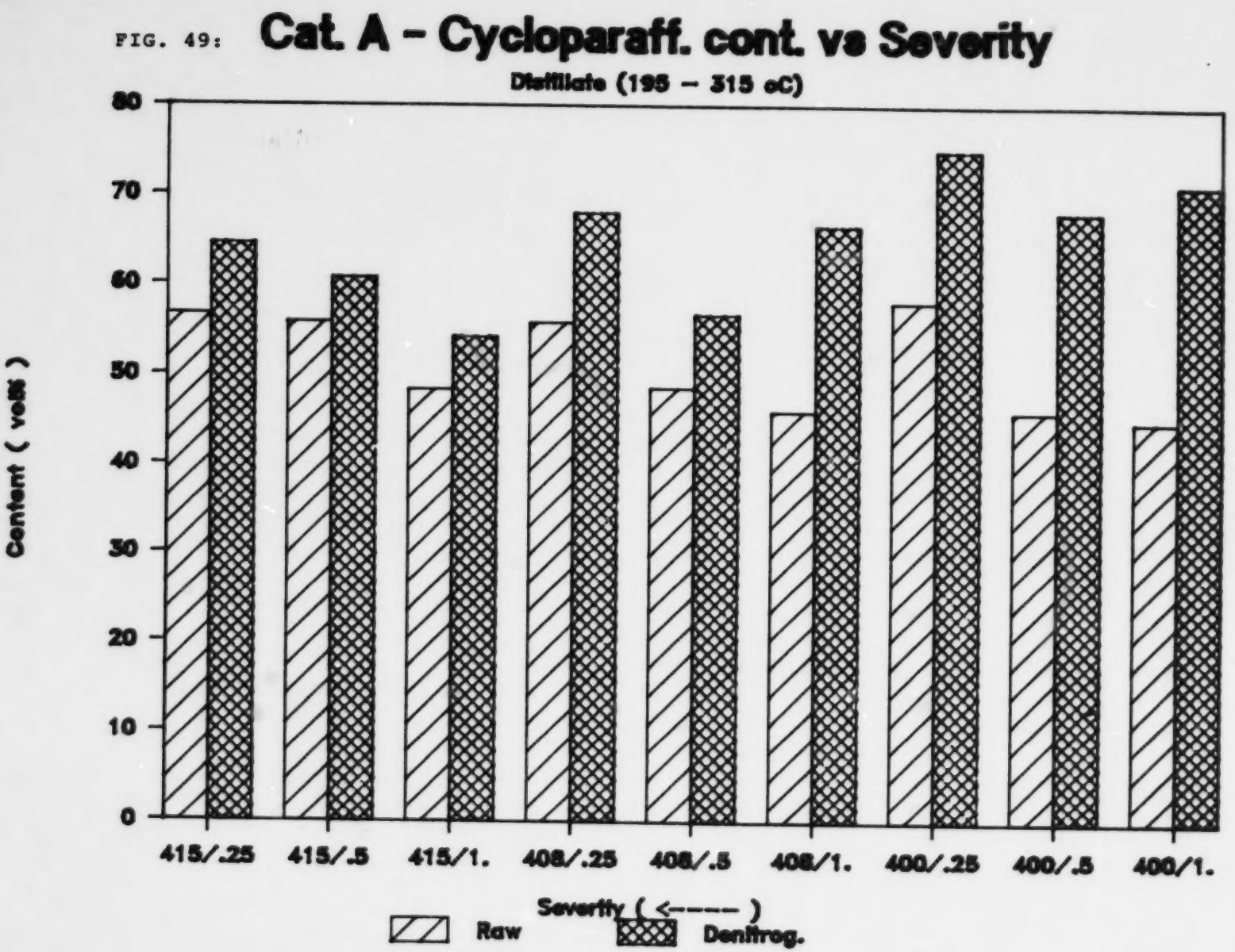

Cat. A - Cycloparaff. cont. vs Severity
Distillate (195 - 315 oC)
Content (vol%)
80
70
60
50
40
30
20
10
0
415/.25
415/.5
415/1.
408/.25
408/.5
408/1.
400/.25
400/.5
400/1.
Severity (<-----)
Raw
Denitrog.

FIG. 50: **Cat. A – Paraffin content vs Severity**

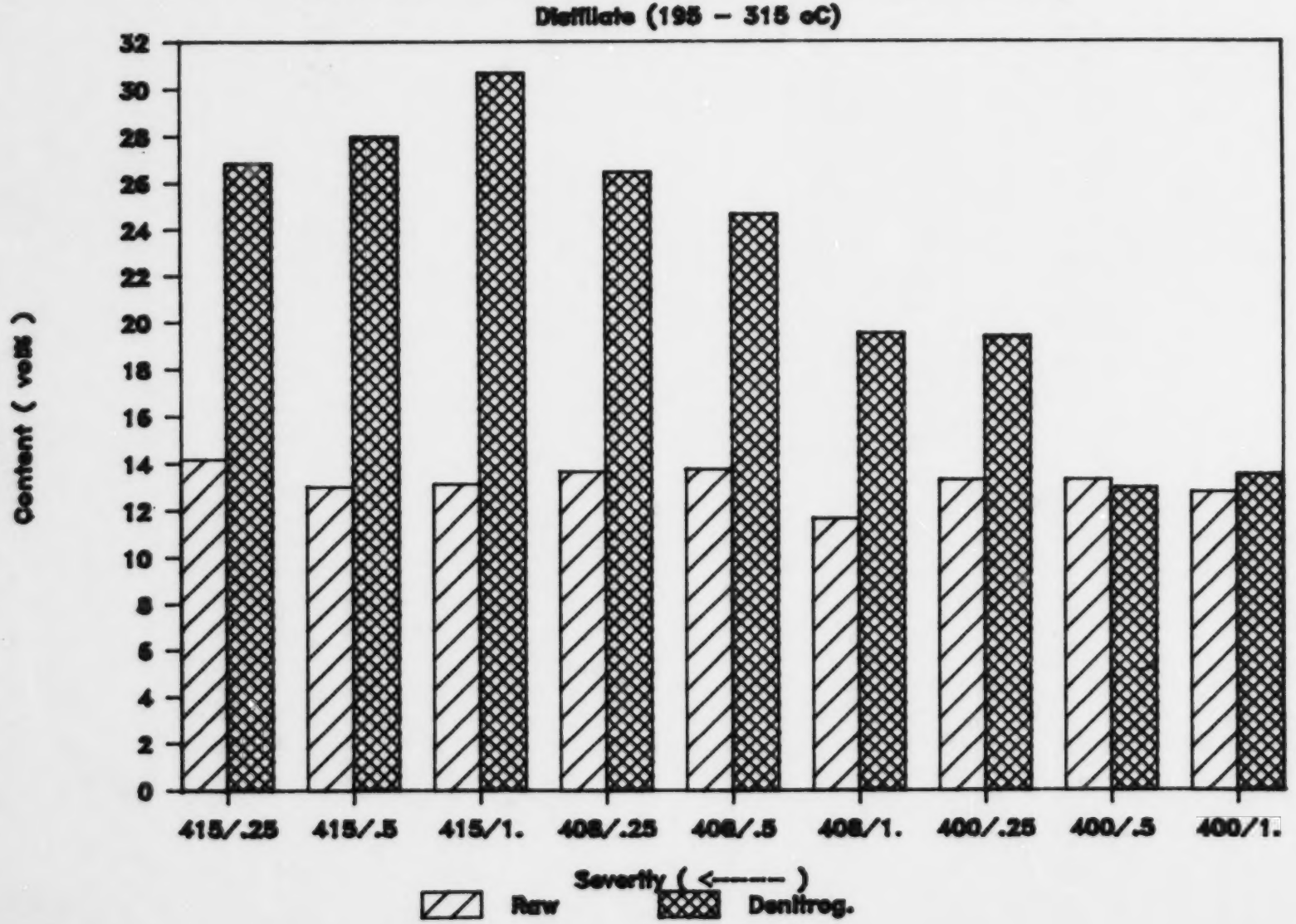


FIG. 51 : **HIGH SEVERITY TESTS**

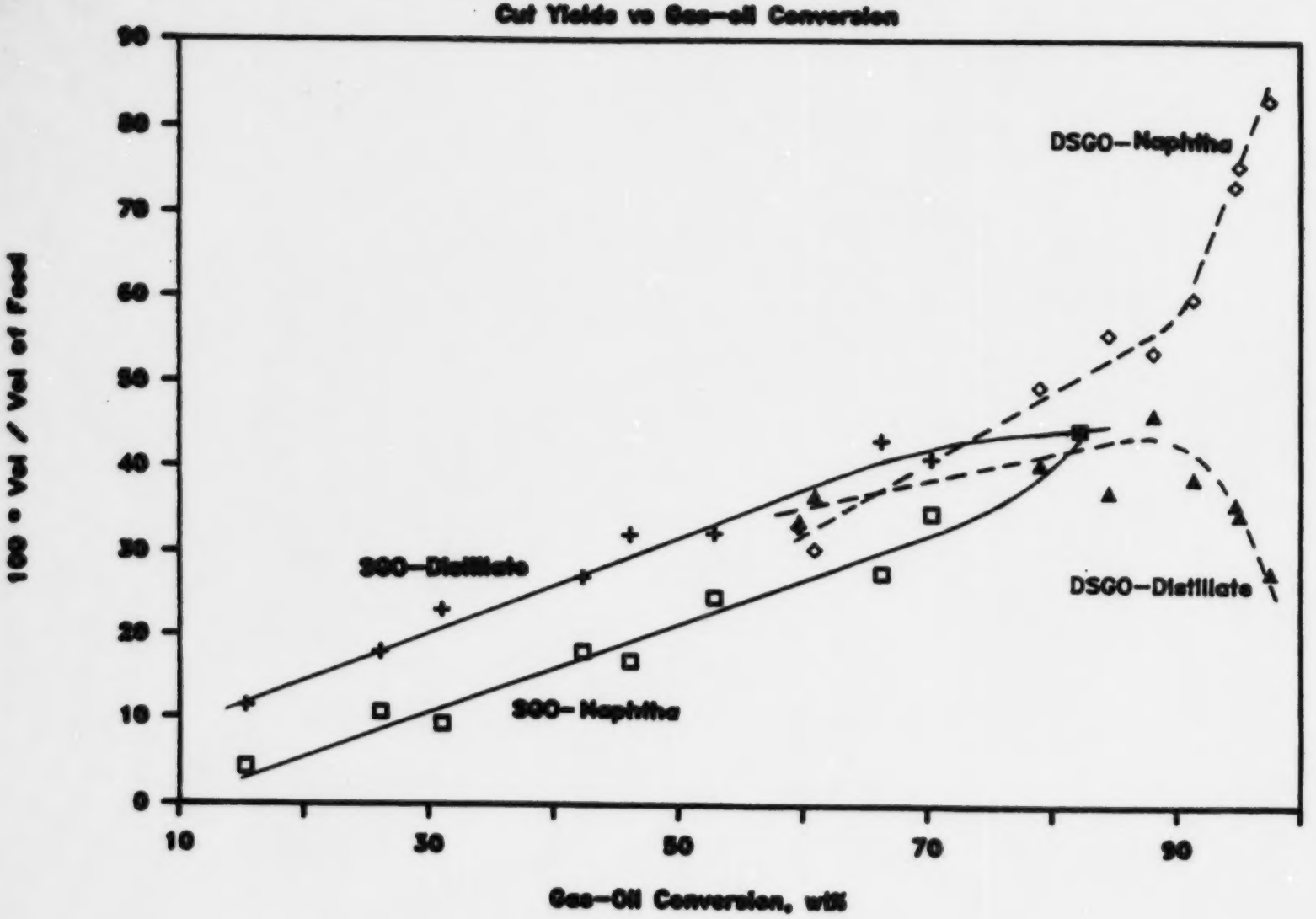


FIG. 52 : **HIGH SEVERITY TESTS - RAW SGO**

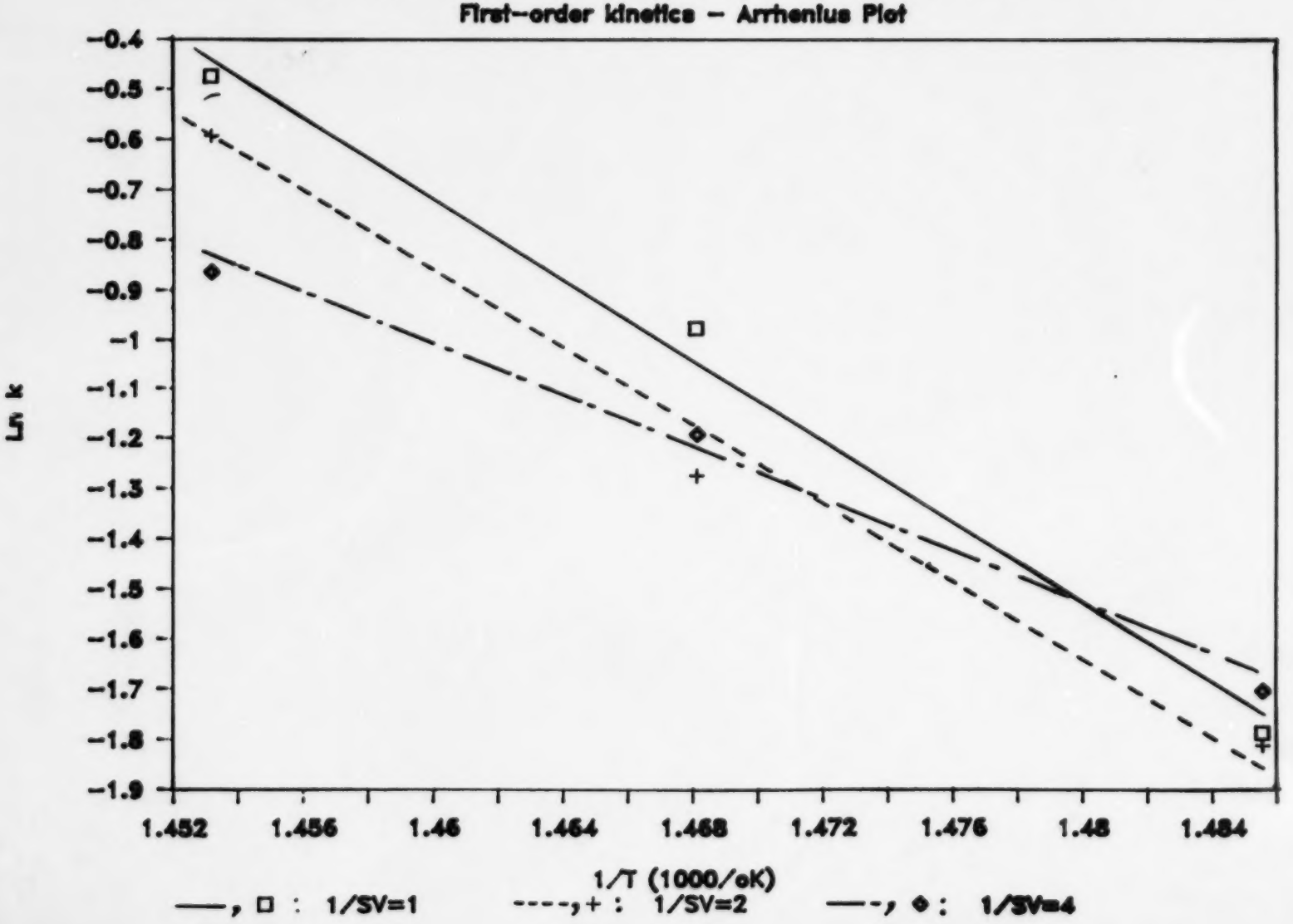


FIG. 53 : HIGH SEVERITY TESTS - RAW SGO
First-order Kinetics - 400 oC

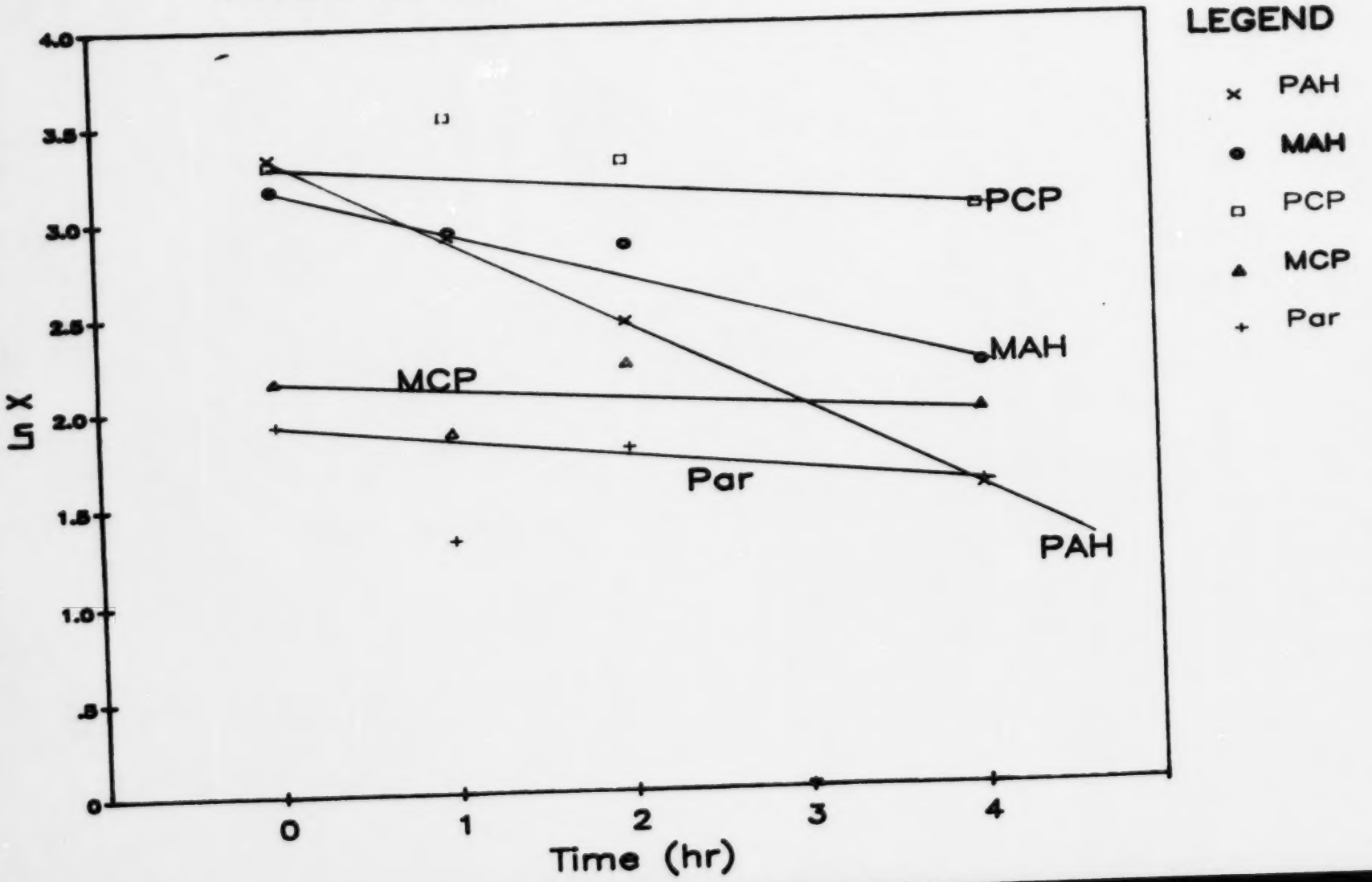


FIG. 54 : HIGH SEVERITY TESTS - RAW SGO
First-order Kinetics - 408 oC

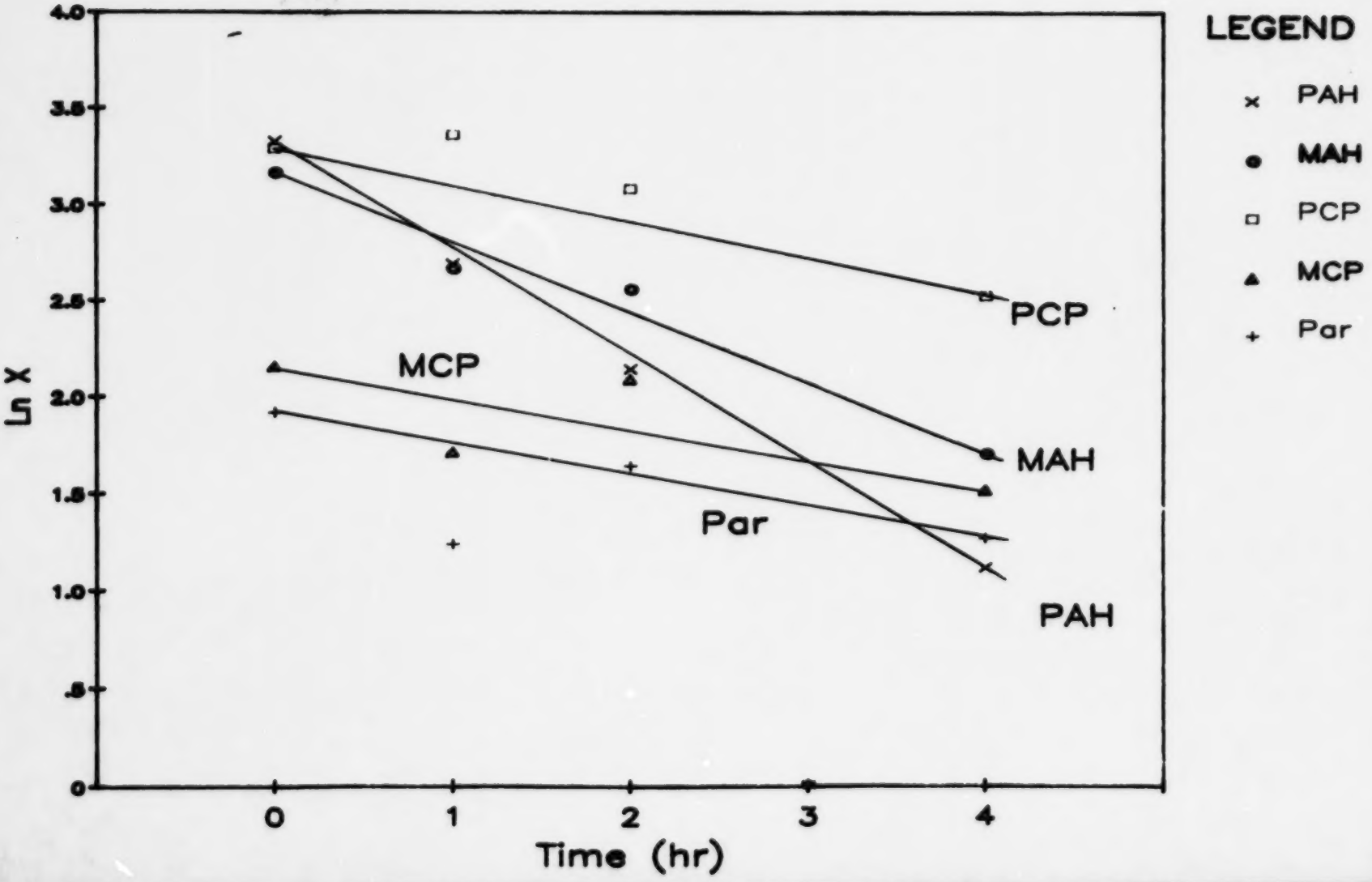


FIG. 55 :

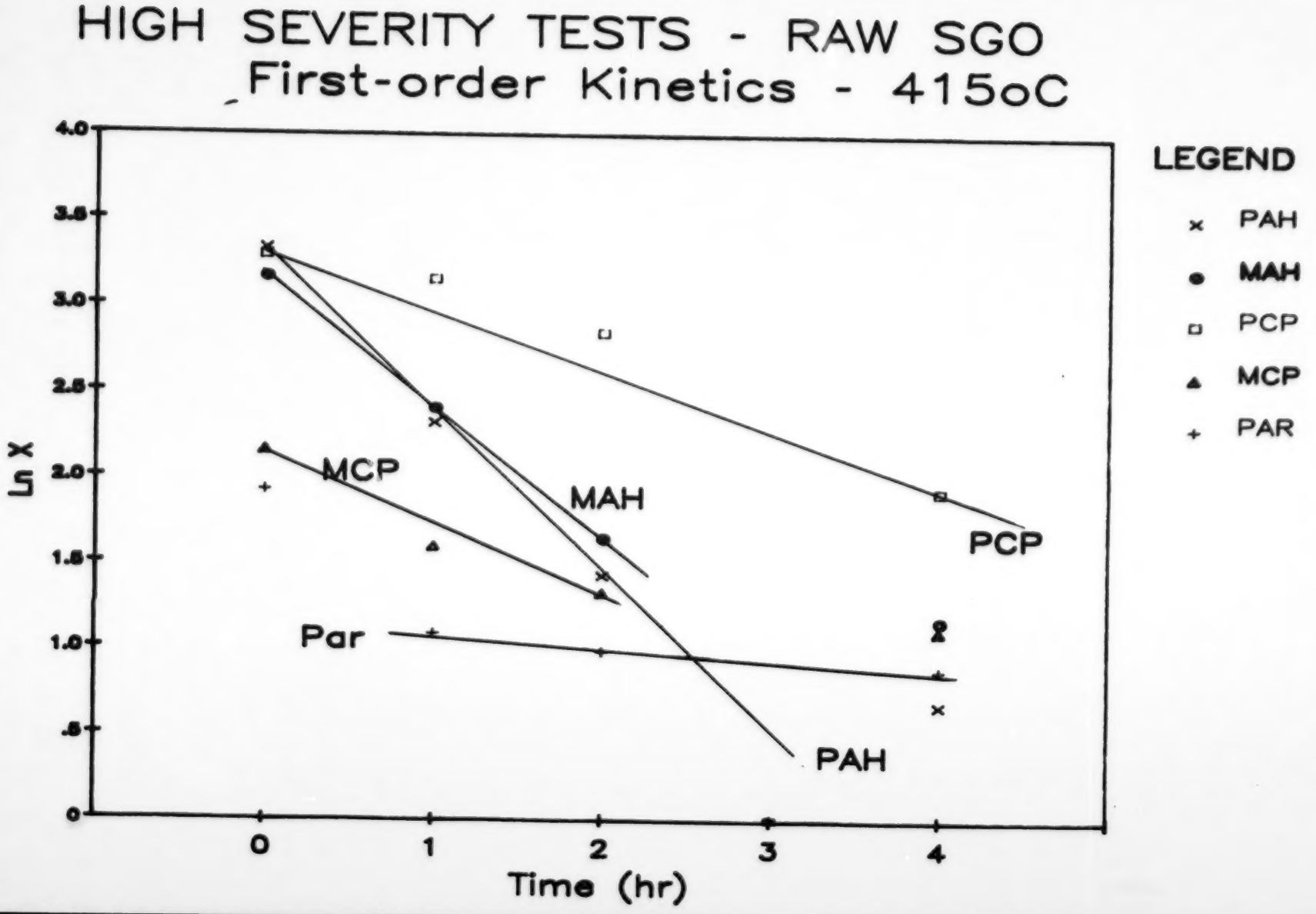
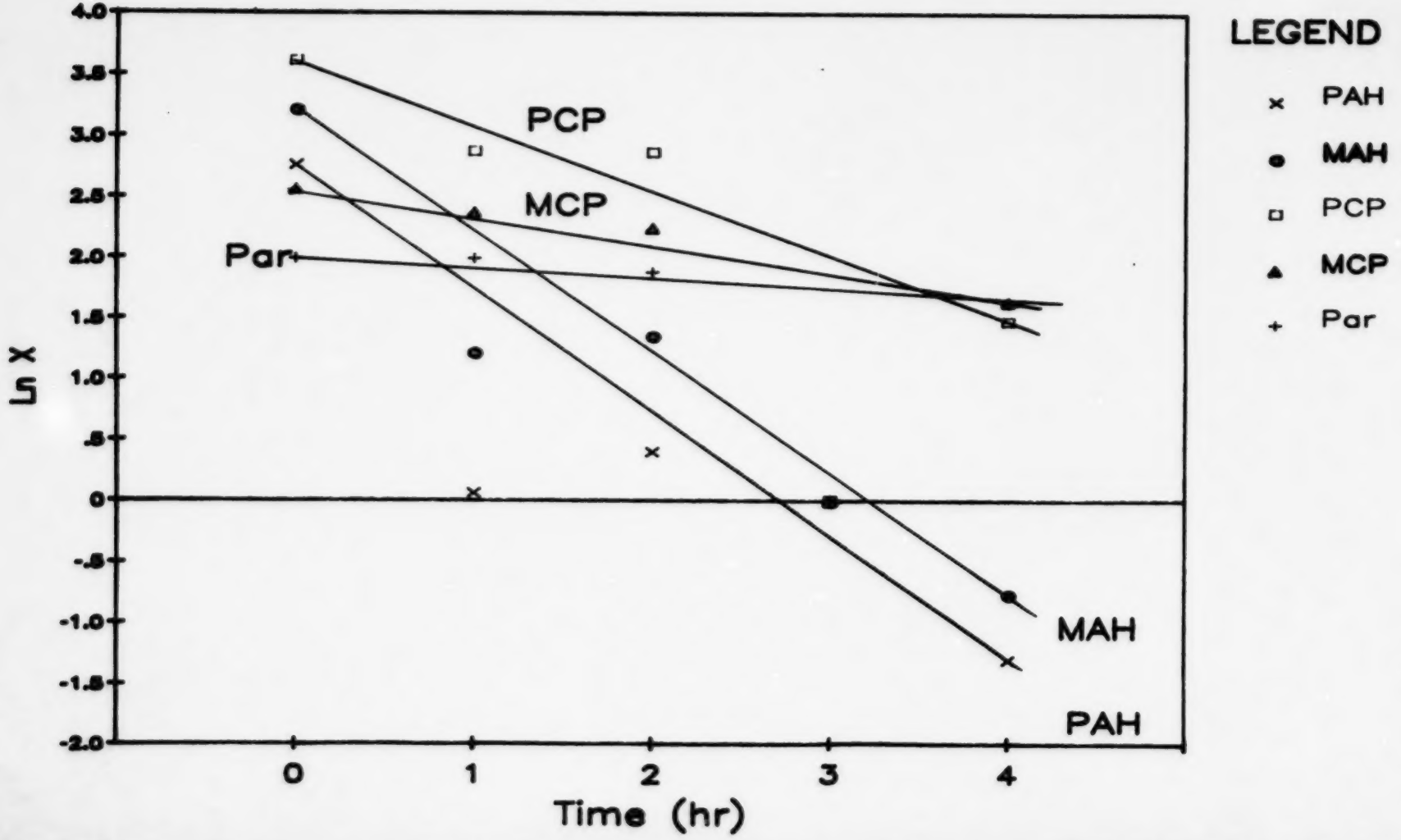

HIGH SEVERITY TESTS - RAW SGO
First-order Kinetics - 415oC
LEGEND
PAH
MAH
PCP
MCP
PAR
Ln X
Time (hr)
MCP
MAH
PCP
Par
PAH
4.0
3.5
3.0
2.5
2.0
1.5
1.0
.5
0
0
1
2
3
4

FIG. 56 :

HIGH SEVERITY TESTS - DENITROGEN. SGO
First-order Kinetics - 400 oC



APPENDIX A

KINETIC STUDY OF SYNCRUDE GAS OIL HYDROCRACKING

SUMMARY

A pseudo kinetic analysis has been performed on the data for hydroconversion of raw Syncrude gas oil (315+) and denitrogenated Syncrude gas oil. Two catalysts, Shell 411 and Cat.A, were studied with both feedstocks.

The pseudo kinetics for sulphur and nitrogen removal were found to be first order. The more active Shell 411 catalyst gave complex kinetics which were rationalized in terms of reactive and unreactive sulphur in the raw Syncrude gas oil. Predictive equations were developed for the sulphur and nitrogen contents for both feeds and both catalysts as a function of time and temperature.

Predictive equations were similarly developed for the aromatic content of the gas oil, the yield of unconverted gas oil and yields of gas plus naphtha and total distillate.

REACTION KINETICS

The purpose of carrying out a kinetic analysis of the removal of S, N, aromatics and of the removal of 315+ material is to be able to predict the quantitation of these components as a function of time and temperature. In general hetero atom removal proceeds at much higher rates than aromatics saturation. Aromatics saturation proceeds much faster than saturate ring cracking. At higher temperatures saturate ring dehydrogenation to aromatics, with the liberation of molecular hydrogen, becomes important.

A study of reaction kinetics is often prerequisite to determining the mechanism of the reactions under study. This is not the case in industrial applications, here, where much more detailed experiments would be required. The kinetic analysis pursued here is empirical and offers little insight into mechanistic fundamentals. The benefits lie in the prediction capability and the potential for scale-up.

SULPHUR REMOVAL

Shell 411 Catalyst, Raw Syncrude Gas Oil (315+)

The major problem in dealing with heteroatom removal in general and sulphur removal in particular lay in the extremely poor repeatability of the analytical values determined for S, N concentrations. The uncertainties reflect poorly on the accuracy of the values. The data manipulation has consequently been selective.

The Syncrude 315+ material had an initial sulphur level of 4100 ppm. This level is the result of coker gas oil having been severely hydrotreated at the Syncrude plant. Sulphur removal is generally regarded as first order in S where the rate of removal if proportional to the amount of S present. For this kind of reactor a typical equation is

$$\ln (P_S/F_S) = -kt \qquad 1.$$

where P_S and F_S are the product and feed sulphur amounts respectively, k is the first order rate constant and t the reciprocal WHSV. In fact, none of the S data for Syncrude 315+ and Shell 411 catalyst (a more active catalyst) fitted equation 1. A plot of $\ln (P_S/F_S)$ or $\ln (P_S)$ against t should be linear. Linearisation of the data was achievable using the criteria and arguments proposed by Gilbert (1) where deviation of pilot plant data from first order kinetics were rationalized in terms of

$$t^{2/3} = - \ln (P_S/F_S) \qquad 2.$$

This effectively linearized curved data for the first order kinetic plots.

A more preferable route for treating the data found here was to define reactive and unreactive sulphur species. Such a procedure (2,3) has been used before where both reactive and unreactive sulphur species obey first order kinetics.

Table 1 shows the raw data for hydrotreating Syncrude 315+ over Shell 411 catalyst. Plotting ln(S) against 1/WHSV gives curved plots indicative of the occurrence of reactive sulphur species and unreactive sulphur species. Extrapolation of the high temperature data to zero time gave the value for unreactive sulphur in the feed of 270 ppm. This means that the reactive sulphur is 3830 ppm. Obviously the slowing down in rate of sulphur removal will only be apparent with an active catalyst operating at a severity sufficient to remove most of the reactive sulphur species.

The equation governing the amount of sulphur in the product is

$$\frac{P_S}{F_S} = \alpha_1 \exp(-k_R t) + \alpha_2 \exp(-k_u t) \qquad 3.$$

where P_S and F_S are the product and feed sulphur ppms respectively

$\alpha_1 \alpha_2$ are the fractions of reactive and unreactive sulphur respectively

k_R, k_u the specific fuel order rate constants for the reactive and unreactive species respectively

t is the time in hours

Using $\alpha_1 = 0.0934$ and $\alpha_2 = 0.066$ with the values of k_u determined from the plot of ln[S] against t, Figure 1, values for k_R were determined by calculating equation 3. Table 2 shows the values for k_u and k_R so determined together with activation energies and pre-exponential A values derived from the Arrhenius plot (Figure 2). The equation for predicting the product sulphur ppm values as a function of temperature, T (°A) and t, h is

$$\text{product sulphur ppm} = 3.83.10^3 \exp[-t\ 5.9\ 10^{10} \exp(-29500/RT)] + 2.70\ 10^2 \exp[-t\ 2.3\ 10^{12} \exp(-37700/RT)] \qquad 4.$$

Shell 411 Catalyst Denitrogenated Syncrude Gas Oil 315+

The previous Syncrude gas oil (315+) was hydrotreated to reduce the S and N levels from 4100 and 1665 ppm respectively to 375 and 394 ppm respectively. The aromatic content was also reduced from 51.6 to 42.7%. At this level of sulphur the kinetics were found to be first order but the analytical data were poorer in repeatability than the previous set. These poor data are plotted in Figure 3. The equation for predicting the product S levels is given by

$$\text{product sulphur, ppm} = \exp[5.6 - 5.4.1.10^{8} \exp(-25200/RT)] \qquad 5.$$

Rate constants and Arrhenius parameters are shown in Table 3. These rates are considerably lower than those for reactive sulphur in the raw gas oil, but somewhat higher than the rates of unreactive sulphur.

Raw Syncrude 315, Cat. "A"

This catalyst was lower in activity in all respects (conversion of S, N, aromatics and gas oil) than Shell 411. Sulphur removal generally did not approach the 270 ppm level of unreactive species and there was no need to invoke that mechanism.

First order S data were generally of better quality than Shell 411 and the denitrogenated gas oil. S levels below 270 ppm (the value of unreactive S in the Shell 411 data) were only achieved at 395°C and 0.5 SV and at 415°C at 1.0 SV. Good first order data are shown in Figure 4 together with the Arrhenius plot. Table 4 shows the values of the rate constants and Arrhenius parameters for Cat."A"and both raw Syncrude gas oil and denitrogenated Syncrude gas oil.

The equations for predicting the S content of the product gas oil for Cat."A"and raw Syncrude gas oil is,

$$\text{Sulphur in product} = \exp[8.3 - t\ 2.2\ 10^{8} \exp(-24600/RT)] \qquad 6.$$

and for the denitrogenated gas oil,

$$\text{Sulphur in product} = \exp[5.6 - t\ 7.9\ 10^{6} \exp(-20800/RT)] \qquad 7.$$

Table 5 summarizes the S conversion data for the two feeds and the two catalysts. Activation energies and pre-exponential factors are shown together with the rates of sulphur removal at 395.0°C for comparative purposes. Similar rate constants are observed for Shell 411 catalyst with denitrogenated feed and for Cat."A" with both feeds.

The more active Shell 411 catalyst appears to remove active sulphur from the raw Syncrude gas oil at a much higher rate than for S removal from the remaining three systems studied here.

Nitrogen Removal

Shell 411 catalyst, raw Syncrude gas oil, 315+. The initial N content of this feed was 1665.0 ppm and the removal of N followed first order kinetics. Treatment of the data was analogous to that for the S conversion data. In general, for this feedstock rates of N removal were higher than those for S removal. Plots of ln[N] against t gave reasonable confirmation of first order behaviour and plots of ln k against 1/T gave a good straight line - line with slope = -E/R and intercept = lnA. Table 6 gives the values so determined for the rate constants at each temperature together with the Arrhenius parameters.

The equation for predicting the N content of the gas oil product as a function of temperature and time was given by

$$\text{Product Nitrogen} = \exp[7.4 - t\ 5.7\ 10^{6}\ \exp(-1800/RT)] \qquad 8.$$

Shell 411 and Denitrogenated Syncrude Gas Oil

Similar treatment for the denitrogenated Syncrude (N-394 ppm) gave calculated rate constants and Arrhenius parameter as shown in Table 7. In general N removal rates were somewhat lower than that in the raw Syncrude gas oil.

The equation for predicting the amount of N in the product is given by

$$\text{Product N (ppm)} = \exp[6.0 - 5\ 1.1\ 10^{7}\ \exp(-19800/RT)] \qquad 9.$$

Catalyst "A" Raw Syncrude Gas Oil and Denitrogenated Syncrude Gas Oil

Cat."A" catalyst exhibited about half the activity of Shell 411 for both these feedstocks. Figure 5 shows, as examples, the first order plots together with Arrhenius plot for N removal from the raw Syncrude gas oil for Cat."A" catalyst. Table 8 shows the Arrhenius parameters and specific rate constants for N removal with Cat."A" catalyst from both feedstocks. These data show that this lower activity catalyst has very similar kinetic parameters for both feedstocks. The appropriate N removal equations are:

Raw Syncrude: $\text{Product N} = \exp[7.4 - t\ 1.7\ 10^{10} \exp(-30100/RT)]$ 10.

DeN. Syncrude: $\text{Product N} = \exp[6.0 - t\ 5.4\ 10^{9} \exp(-28600/RT)]$ 11.

Table 9 summarizes the N kinetic results for the two feedstocks and two catalysts. Data shown include activation energies and pre-exponential factors together with (for comparison) specific rate constants at 395°C. Data indicate that Shell 411 is clearly a more active catalyst for nitrogen removal. Furthermore this catalyst is less temperature dependent than Cat."A" - this is often a processing benefit.

Thus for both removal of S and of N Shell 411 is more active, particularly for N removal.

Conversion Kinetics

It if often beneficial to be able to model aromatic conversion, gas oil conversion and the rate of production of products in order to be able to predict these dependent values in hydrocracking processes. In general conversion of 315+ material is first order in gas oil concentration. Results from gas oil hydrocracking (4) over GC-36 in lube production indicated that different gas oils had different rate constants but a fairly constant activation energy of around 57.0 kcals/mole. Differences in pre-exponential factor were closely and predictably related to viscosities of the feedstock. First order dependence would imply an equation of the form

$$\ln \left(\frac{\text{Gas Oil Prod}}{\text{Gas Oil Feed}}\right) = -kt$$

which may be equated with that developed for lube hydrocracking namely

$$\ln \left(\frac{\text{Yield 315+}}{100}\right) = -kt.$$

This form was used to study and model both the cracking of gas oil (315+) and decay of total aromatics from the gas oil feedstock.

Conversion Kinetics for Raw and Denitrogenated Syncrude Gas Oil, Shell 411 Catalyst

The data in Table 1 showing the appropriate input values were used to model the conversion of gas oil and aromatics. Figure 6 shows the first order plots for decay of gas oil feedstock and aromatics in feedstock for Shell 411 and the raw Syncrude feed. At 415°C the aromatic content in the product gas oil increased over the value at 395°C. This effect has been quantified and discussed (5) and is the result of equilibrium driven dehydrogenation of the polycyclic saturate ring compounds to aromatic compounds. The rate constants found here were plotted in the standard Arrhenius form to give activated energies and pre-exponential factors. These are shown together with data for the denitrogenated Syncrude 315+ in Table 10.

These data indicate that the more aromatic raw Syncrude (315+) gas oil undergoes hydrogenation more readily than the denitrogenated gas oil. Both feedstocks behave similarly towards cracking.

In trying to predict the yields of distillate and lighter products an interesting correlation was found between conversion and yields of gas plus naphtha and yield of total distillate. Conversion may be readily predicted using the two equations 12 and 13 below.

Shell 411 Syncrude (315+)

$$\text{Yield of 315+ gas oil} = \exp\left[4.605 - t\ 9.6\ 10^{14} \exp(-47700/RT)\right] \qquad 12.$$

$$\text{Conversion} = 100 - \exp\left[4.605 - t\ 9.6\ 10^{14} \exp(-47700/RT)\right]$$

Shell 411 denitrogenated Syncrude 315+

$$\text{Yield of 315+ gas oil} = \exp[4.605 - t\ 4.0\ 10^{15} \exp(-50000/RT)] \qquad 13.$$

$$\text{Conversion} = 100 - \exp[4.605 - t\ 4.0\ 10^{15} \exp(-50000/RT)[$$

Figure 7 shows data relating the yield of naphtha + gas and distillate to conversion. All the data from Table 1 are represented here for both catalysts and both feedstocks. The data show that the yield of distillate is always two-thirds of the conversion and the yield of naphtha + gas one-third of the conversion.

Catalyst "A", Syncrude 315 and Denitrogenated Syncrude 315+

The data were closely similar to the 411 catalyst. Table 11 summarizes the Arrhenius data and rate constants. There is an indication here that Cat."A" at higher temperatures, (415°C, only one data point) finds the denitrogenated gas oil more easy to crack then the raw Syncrude gas oil. Such an observation was not made with the 411 catalyst. Similarly the aromatics are more easily removed at 415°C with the denitrogenated feed as compared with the raw VGO. The data at other severities indicate equal reactivities of the feedstock.

The equations for predicting the yield of gas oil and conversion are shown 14, 15.

Catalyst "A", Syncrude Raw Gas Oil (315+)

$$\text{Yield of 315+ gas oil} = \exp[4.605 - t\ 7.2\ 10^{15} \exp(-50800/RT)] \qquad 14.$$

$$\text{Conversion} = 100 - \exp[4.605 - t\ 7.2\ 10^{15} \exp(50800/RT)]$$

Catalyst "A", Denitrogenated Syncrude Gas Oil (315+)

$$\text{Yield of 315+ gas oil} = \exp[4.605 - t\ 1.2\ 10^{20} \exp(-63500/RT)] \qquad 15.$$

$$\text{Conversion} = 100 - \exp[4.605 - t\ 1.2\ 10^{20} \exp(-63500/RT)]$$

Finally, Table 12 summarizes and reiterates the pseudo kinetic data together with the appropriate equations for predicting S, N, aromatics, yield of gas oil, distillate, naphtha + gas as a function of temperature (°A) and time (h).

I. P. Fisher

IPF/gp
Attach.

References

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TABLE 1

HYDROCRACKING RAW SYNCRUDE GAS OIL (315+)
AND DENITROGENATED SYNCRUDE OVER SHELL 411 CATALYST AT 2750 psi H_2

	Feed	Raw Syncrude 315+												
Temp. °C		---- 395 ----			---- 383 ----			---- 370 ----			---- 360 ----			415
S.V. h^{-1}		0.5	1.0	2.0	0.5	1.0	2.0	0.5	1.0	2.0	0.5	1.0	2.0	1.0
S, ppm	4100.0	27.0	90.0	133.0	103.0	117.0	217.0	117.0	217.0	502.0	160.0	330.0	820.0	105.0
N, ppm	1665	2.9	5.2	160.0	5.8	127.0	490.0	21.9	83.3	292.0	62.0	185.0	483.0	3.6
Yields, mass % FF														
Gas Oil	100.0	62.0	74.1	85.2	83.3	88.3	92.7	90.4	91.7	96.6	100.0	100.0	100.0	55.1
Distillate	0	24.6	17.1	9.0	11.3	7.8	5.0	6.5	3.7	2.3				27.5
Gas + Naphtha	0	13.4	8.8	5.8	5.4	3.9	2.8	3.1	4.6	1.1				17.4
Aromatics	51.6	4.7	13.7	27.6	12.1	26.9	35.2	17.4	32.4	43.2				12.2
Conversion, %	0	38.0	25.9	14.8	16.7	11.7	7.3	9.6	8.3	3.4				44.9
		Denitrogenated 315+ Syncrude												
S, ppm	375.0		62.0	82.0	69.0	89.0	111.0	60.0	105.0	154.0	90.0	156.0	146.0	70.0
N, ppm	394.0	80.0*	10.5	0.6	2.3	31.9	183.0	21.7	54.0	103.0	20.5	69.0	135.0	1.4
Yields, mass % FF														
Gas Oil	100.0	72.0	84.3	91.7	85.9	92.2	95.1	93.0	96.5	97.9	100.0	100.0	100.0	54.8
Distillate	0	19.7	10.3	5.5	10.6	5.4	2.7	5.5	3.3	1.8				29.1
Gas + Naphtha	0	8.3	5.4	2.8	3.5	2.4	2.2	1.5	0.2	0.3				16.1
Aromatics	42.7	7.9	18.2	25.7	9.9	25.0	31.2	21.4	33.3	35.4				10.8
Conversion	0	28.0	15.7	8.3	14.1	7.8	4.9	7.0	3.5	2.1				45.2

TABLE 1 Cont'd

HYDROCRACKING RAW SYNCRUDE GAS OIL (315+)
AND DENITROGENATED SYNCRUDE OVER CATALYST "A" AT 2750 psi H_2

	Feed												
		Raw Syncrude 315+											
Temp. °C		- - - - 395 - - - -			- - - - 383 - - - -			- - - - 370 - - - -			- - - - 360 - - - -			415
S.V. h^{-1}		0.5	1.0	2.0	0.5	1.0	2.0	0.5	1.0	2.0	0.5	1.0	2.0	1.0
S, ppm	4100.0	121.0	506.0	1241.0	304.0	947.0	1660.0	623.0	1473.0	2164.0	1146.0	1843.0	2587.0	120.0
N, ppm	1665	28.0	210.0	585.0	96.0	436.0	732.0	253.0	635.0	993.0	461.0	802.0	1264.0	17.0
Yields, mass % FF														
Gas Oil		70.9	87.1	92.2	85.8	93.2	96.6	94.0	96.9	98.0	100.0	100.0	100.0	58.1
Distillate		18.5	9.0	6.7	9.3	5.5	2.8	3.9	1.7	1.4				27.2
Gas + Naphtha		10.3	3.9	1.1	4.9	1.3	0.6	2.1	1.4	0.6				17.7
Aromatics		18.9	32.7	34.9	29.4	41.6	45.3	34.5	46.1	47.4				16.6
Conversion, %		29.1	12.9	7.8	14.2	6.8	3.4	6.0	3.1	2.0				41.9
		Denitrogenated 315+ Syncrude												
Temp. °C		- - - - 395 - - - -			- - - - 383 - - - -			- - - - 370 - - - -			- - - - 360 - - - -			415
S.V. h^{-1}		0.5	1.0	2.0	0.5	1.0	2.0	0.5	1.0	2.0	0.5	1.0	2.0	1.0
S, ppm	375.0	68.0	110.0	193.0	64.3	148.0	253.0	114.0	210.0	257.0	143.0	218.0	313.0	1.5
N, ppm	394.0	0.5	43.0	126.0	56.0	61.0	213.0	80.2	171.0	209.0	118.0	205.0	337.0	2.2
Yields, mass % FF														
Gas Oil	100.0	66.9	88.8	94.9	90.3	93.0	97.7	95.0	97.8	98.1	100.0	100.0	100.0	43.3
Distillate	0	22.4	6.7	3.7	7.1	4.8	1.9	4.4	2.1	1.4				35.4
Gas + Naphtha	0	10.7	4.5	1.4	2.6	2.2	0.4	0.6	0.2	0.5				21.3
Aromatics	42.7	10.5	27.3	33.4	25.9	30.2	35.1	29.6	30.1	34.5				6.1
Conversion	0	33.1	11.2	5.13	9.7	7.0	2.3	5.0	2.2	1.9				54.7

TABLE 2

ARRHENIUS CONSTANTS AND SPECIFIC RATE CONSTANTS FOR REMOVAL OF REACTIVE AND UNREACTIVE SULPHUR
SHELL 411 CATALYST, SYNCRUDE 315+ VGO

Temp.	k_R	k_u
395	13.0*	1.0
383	9.2	0.5
370	5.3	0.4
360	3.8	0.3

* Extrapolated

$E_{REACTIVE}$ = 29.5 kcals/mole $A_{REACTIVE}$ = $5.9\ 10^{10}$

$E_{UNREACTIVE}$ = 37.7 kcals/mole $A_{UNREACTIVE}$ = $2.3\ 10^{12}$

TABLE 3

ARRHENIUS CONSTANTS AND SPECIFIC RATE CONSTANTS FOR S REMOVAL.
SHELL 411 CATALYST
DENITROGENATED SYNCRUDE 315+ VGO

Temp.	k, h^{-1}
415	3.0
395	2.0
383	
370	1.1
360	0.8

E = 25.2 kcals/mole

A = $4.1\ 10^{8}$

TABLE 4

ARRHENIUS CONSTANTS AND SPECIFIC RATE CONSTANTS FOR S REMOVAL. CATALYST "A", RAW SYNCRUDE GAS OIL 315+ AND DENITROGENATED SYNCRUDE 315+ VGO

Temp. °C	k(Syncrude) h^{-1}	k(Denitrogenated) h^{-1}
415	3.3	1.9
395	1.9	1.2
383	1.4	0.9
370	1.0	0.6
360	0.7	0.5
	E = 24.6 kcal/mole	E = 20.8 kcal/mole
	A = 2.2 10^8	A = 7.9 10^6

TABLE 5

S CONVERSION KINETICS SUMMARY

ARRHENIUS PARAMETERS AND RATE CONSTANTS AT 395.0°C

Catalysts	Feed	E_{ACT} kcal/m		A	k(395.0) h^{-1}
Shell 411	Syncrude	29.5	(R)	$5.9\ 10^{10}$	13.0
Shell 411	Syncrude	37.7	(u)	$2.3\ 10^{12}$	1.0
Shell 411	Denit. Syncrude	25.2		$4.1\ 10^{8}$	2.0
Cat."A"	Syncrude	24.6		$2.2\ 10^{8}$	1.9
Cat."A"	Denit. Syncrude	20.8		$7.9\ 10^{6}$	1.2

TABLE 6

ARRHENIUS PARAMETERS AND SPECIFIC RATE CONSTANTS FOR SHELL 411 REMOVING NITROGEN FROM RAW SYNCRUDE GAS OIL (315+)

Temp.	k
415	6.2
395	4.2
383	2.9
370	2.3
360	2.9

E = 18.8 kcals/mole

A = $5.7\ 10^6$

TABLE 7

ARRHENIUS PARAMETERS AND SPECIFIC RATE CONSTANTS
FOR N REMOVAL FROM DENITROGENATED SYNCRUDE
GAS OIL SHELL 411 CATALYST

Temp.	k
415	5.6
395	3.5
383	2.6
370	1.9
360	1.6

E = 19.8 kcals/mole

$A = 1.1\ 10^{7}$

TABLE 8

ARRHENIUS PARAMETERS AND SPECIFIC RATE CONSTANTS FOR N REMOVAL FROM BOTH RAW AND DENITROGENATED SYNCRUDE GAS CATALYST "A"

Temp.	k(Syncrude)	k(Denit. Syncrude)
415	4.6	5.2
395	2.0	2.0
383	1.5	1.2
370	0.9	0.9
360	0.6	0.6

E = 30.1 kcals/m

$A = 1.7\ 10^{10}$

E = 28.6 kcals/mole

$A = 5.4\ 10^{9}$

TABLE 9

N CONVERSION KINETICS SUMMARY

ARRHENIUS PARAMETERS AND RATE CONSTANTS AT 395.0°C

Catalysts	Feed (315+)	E_{ACT} kcal/m	A	k(395.0) h^{-1}
Shell 411	Syncrude	18.8	$5.7\ 10^{6}$	4.2
Shell 411	Denit. Syncrude	19.8	$1.1\ 10^{7}$	3.5
Cat."A"	Syncrude	30.1	$1.7\ 10^{10}$	2.0
Cat."A"	Denit. Syncrude	28.6	$5.4\ 10^{9}$	2.0

TABLE 10

ARRHENIUS PARAMETERS AND SPECIFIC RATE CONSTANTS
FOR AROMATIC REMOVAL AND GAS OIL YIELD. SHELL 411
CATALYST SYNCRUDE 315+ AND DENITROGENATED SYNCRUDE 315+

	Syncrude (315+)		Denit. Syncrude (315+)	
°C	$k_{Arom.}$	k_{315+}	$k_{Arom.}$	k_{315+}
415	--	0.6	--	0.6
395	1.2	0.3	0.9	0.2
383	0.9	0.1	0.7	(0.08)
370	0.5	(0.07)	0.3	(0.04)
$E_{kcal/mole}$	30.8	47.7	32.0	50.0
A	$1.4\ 10^{10}$	$9.6\ 10^{14}$	$2.8\ 10^{10}$	$4.0\ 10^{15}$

TABLE 11

CATALYST "A". ARRHENIUS PARAMETERS AND SPECIFIC RATE CONSTANTS FOR GAS OIL CONVERSION AND AROMATICS REMOVAL SYNCRUDE (315+) AND DENITROGENATED SYNCRUDE (315+)

	Syncrude (315+)		Denit. Syncrude (315+)	
°C	$k_{Arom.}$	k_{315+}	$k_{Arom.}$	k_{315+}
415	1.1	0.5	2.0	0.8
395	0.6	0.2	0.6	0.2
383	0.3	0.1	0.4	(0.07)
370	0.2	0.04	0.2	(0.03)
E, kcal/mole	41.3	50.8	42.6	63.5
A	$1.8\ 10^{13}$	$7.2\ 10^{15}$	$6.5\ 10^{13}$	$1.2\ 10^{20}$

TABLE 12

SUMMARY OF KINETIC DATA

Catalyst/Feed	E(kcal/mole)	A	k(395), h^{-1}	Equation
1. S Removal				
411 Syncrude (R)	29.5	$5.9\ 10^{10}$	13.0	$3.83\ 10^{3}\ \exp[-t\ 5.9\ 10^{10}\exp(-29500/RT)]$
411 Syncrude (u)	37.7	$2.3\ 10^{12}$	1.0	$+\ 2.70\ 10^{2}\ \exp[-t\ 2.3\ 10^{12}\exp(-37700/RT)]$
411 Denit. Syncrude	25.2	$4.1\ 10^{8}$	2.0	$\exp[5.6-t\ 4.1\ 10^{8}\exp(-25200/RT)]$
Cat."A" Syncrude	24.6	$2.2\ 10^{8}$	1.9	$\exp[8.3-t\ 2.2\ 10^{8}\exp(-24600/RT)]$
Cat."A" Den. Syncrude	20.8	$7.9\ 10^{6}$	1.2	$\exp[5.6-t\ 7.9\ 10^{6}\exp(-20800/RT)]$
2. N Removal				
411 Syncrude	18.8	$5.7\ 10^{6}$	4.2	$\exp[7.4-t\ 5.7\ 10^{6}\exp(-18800/RT)]$
411 Den. Syncrude	19.8	$1.1\ 10^{7}$	3.5	$\exp[6.0-t\ 1.1\ 10^{7}\exp(-19800/RT)]$
Cat."A" Syncrude	30.1	$1.7\ 10^{10}$	2.0	$\exp[7.4-t\ 1.7\ 10^{10}\exp(-30100/RT)]$
Cat."A" Den. Syncrude	28.6	$5.4\ 10^{9}$	2.0	$\exp[6.0-t\ 5.4\ 10^{9}\exp(-28600/RT)]$
3. Aromatics Removal				
411 Syncrude	30.8	$1.4\ 10^{10}$	1.2	$\exp[3.94-t\ 1.4\ 10^{10}\exp(-30800/RT)]$
411 Den. Syncrude	32.0	$2.8\ 10^{10}$	0.9	$\exp[3.75-t\ 2.8\ 10^{10}\exp(-32000/RT)]$
Cat."A" Syncrude	41.3	$1.8\ 10^{13}$	0.6	$\exp[3.94-t\ 1.8\ 10^{13}\exp(-41300/RT)]$
Cat."A" Den. Syncrude	42.6	$6.5\ 10^{13}$	0.6	$\exp[3.75-t\ 6.5\ 10^{13}\exp(-42600/RT)]$
4. Gas Oil Yield/Feed				
411 Syncrude	47.7	$9.6\ 10^{14}$	0.3	$\exp[4.605-t\ 9.6\ 10^{14}\exp(-47700/RT)]$
411 Den. Syncrude	50.0	$4.0\ 10^{15}$	0.2	$\exp[4.605-t\ 4.0\ 10^{15}\exp(-50000/RT)]$
Cat."A" Syncrude	50.8	$7.2\ 10^{15}$	0.2	$\exp[4.605-t\ 7.2\ 10^{15}\exp(-50800/RT)]$
Cat."A" Den. Syncrude	63.5	$1.2\ 10^{20}$	0.2	$\exp[4.605-t\ 1.2\ 10^{20}\exp(-63500/RT)]$

5. Yield of distillate, % = 0.67 * Conversion %
   Yield of Naphtha + Gas % = 0.33 * Conversion %

FIGURE 1

FIRST ORDER PLOT FOR S REMOVAL
FROM SYNCRUDE 315+ OVER SHELL 411
REACTIVE / UNREACTIVE SULPHUR

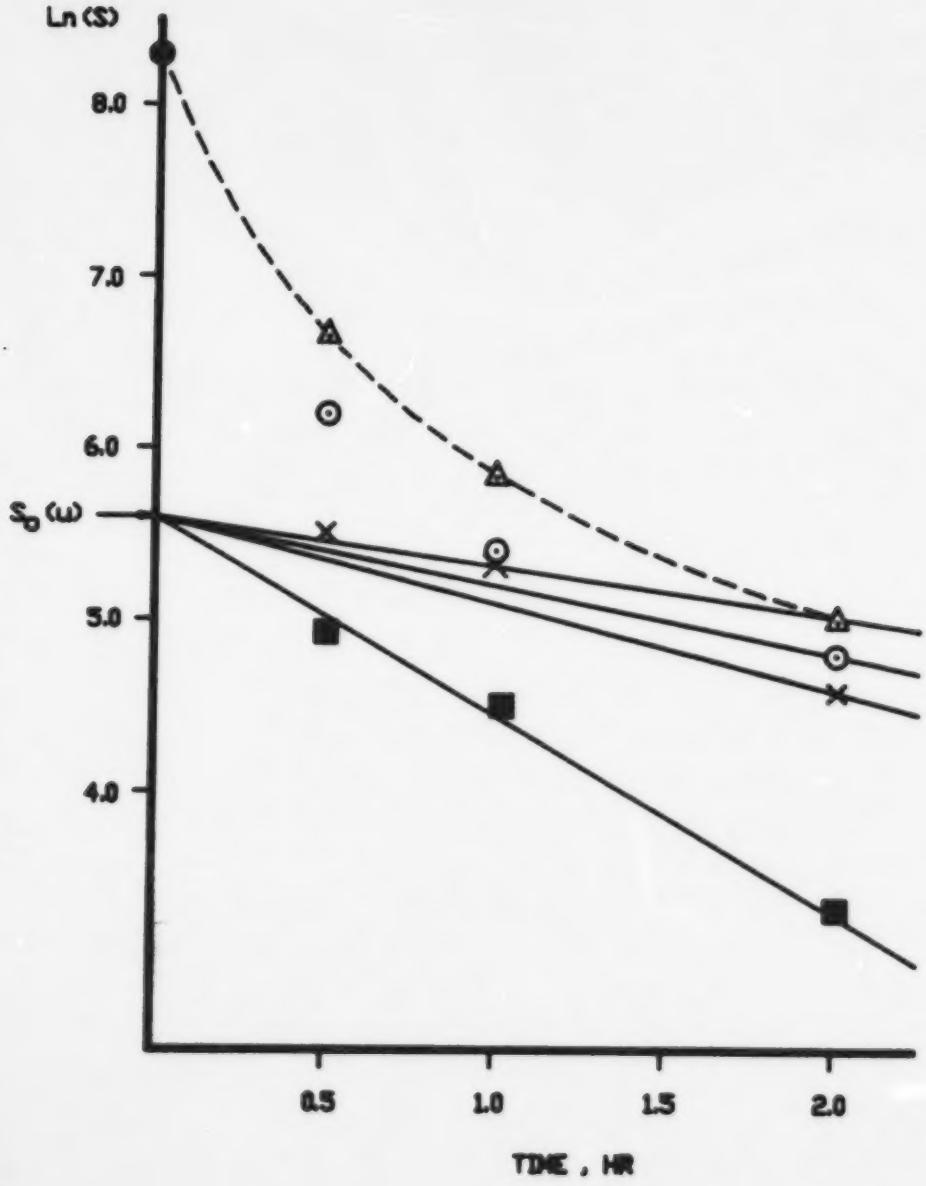

FIGURE 2

ARRHENIUS PLOT FOR REACTIVE AND ANREACTIVE SULPHUR IN SYNCRUDE 315+ GAS OIL

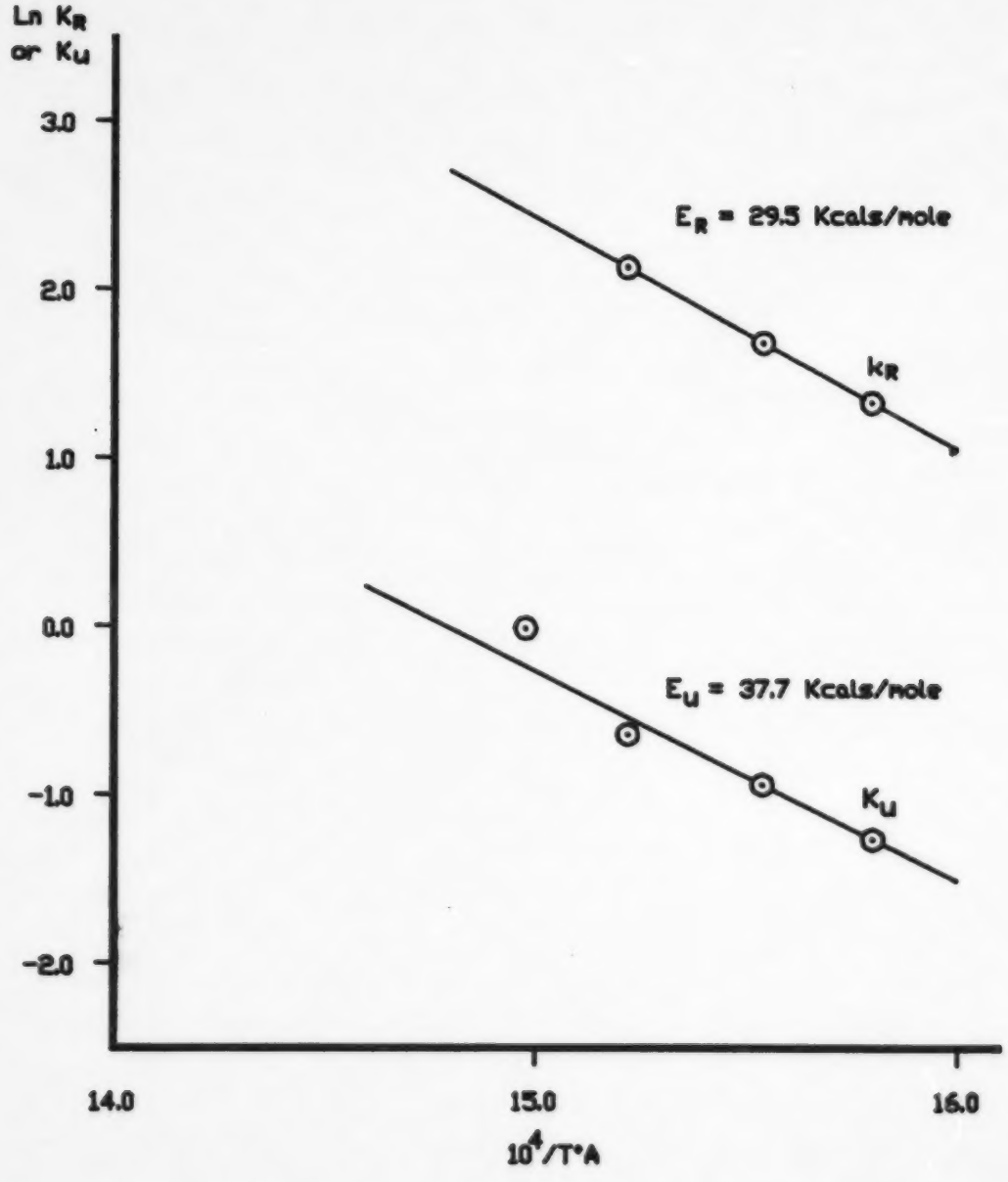

FIGURE 3

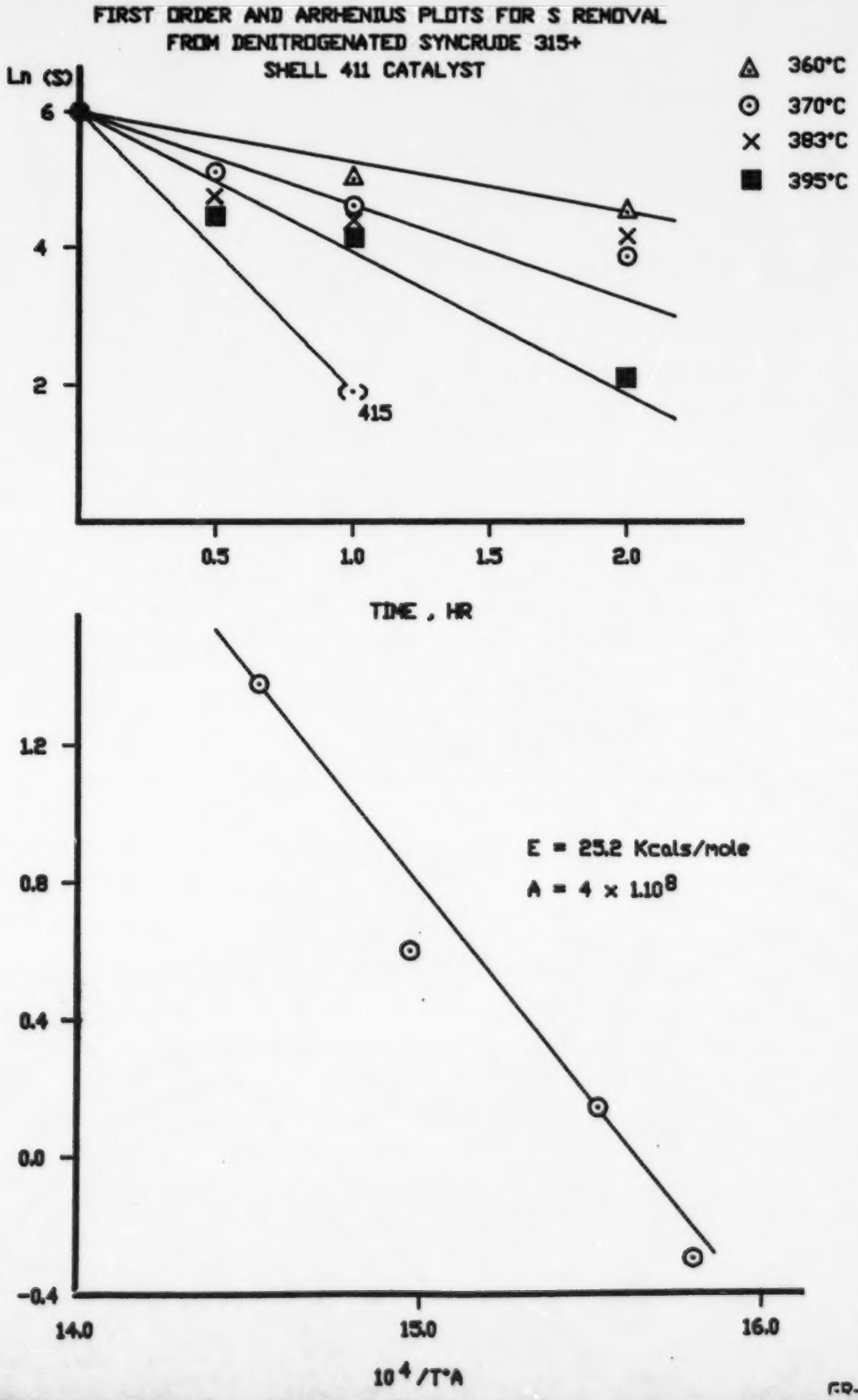

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FIGURE 4

CAT. "A" FIRST ORDER S REMOVAL , ARRHENIUS PLOT
FOR SYNCRUDE 315+

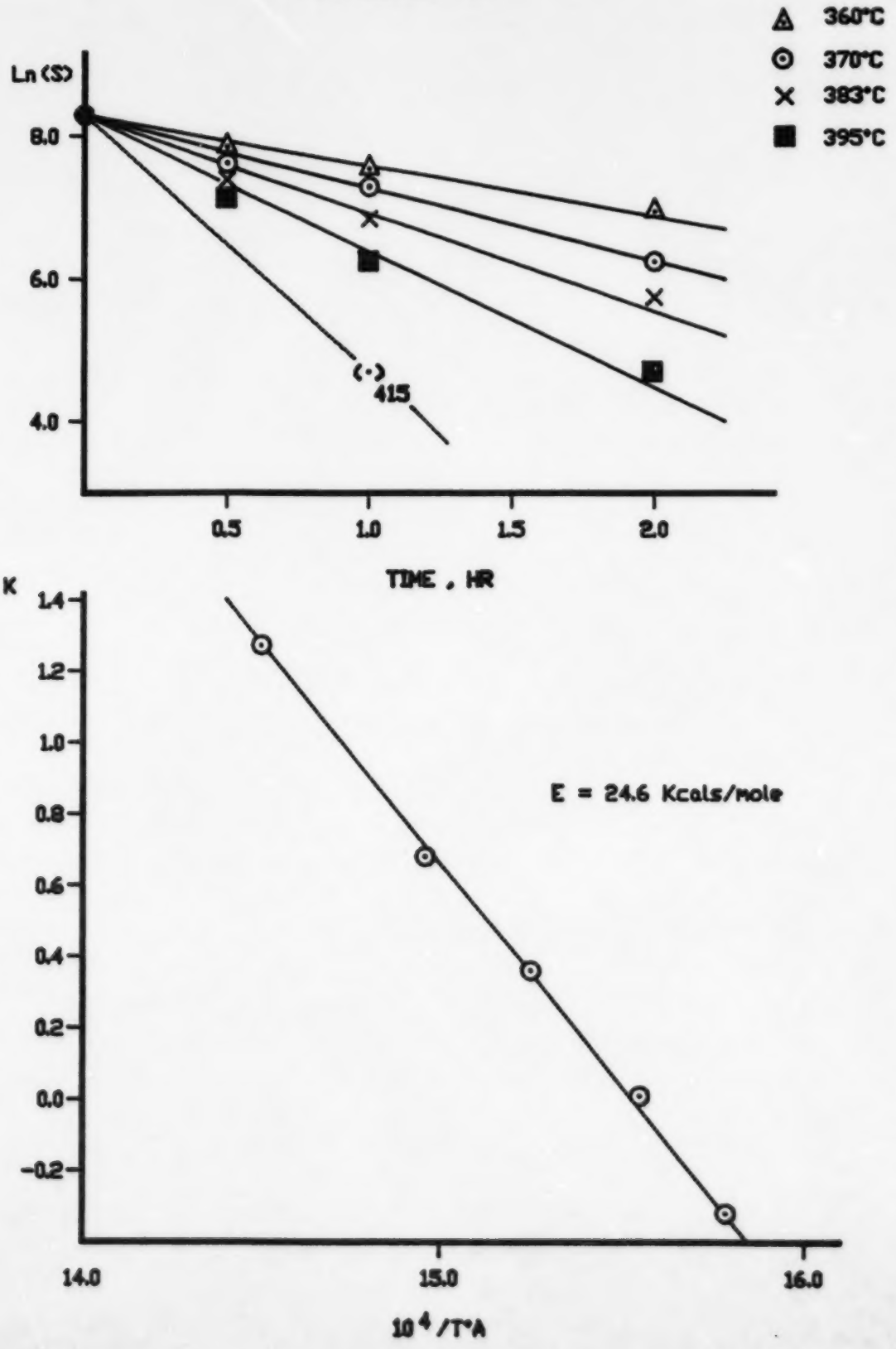
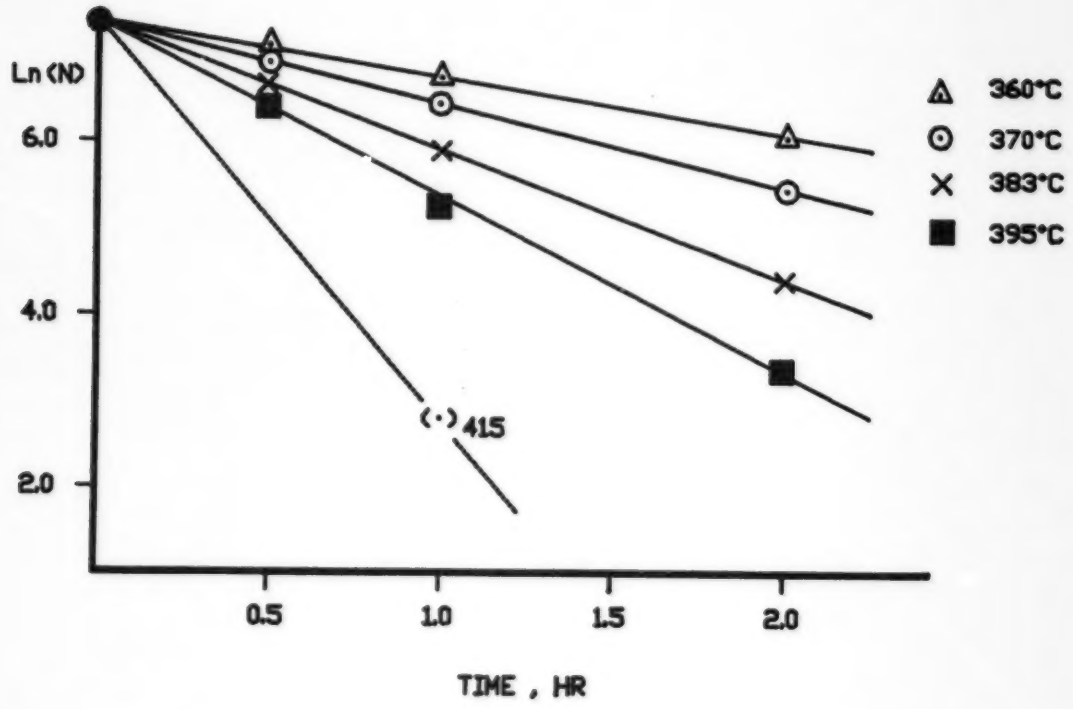


FIGURE 5

ARRHENIUS PLOT AND FIRST ORDER PLOTS FOR N REMOVAL
FROM ROW SYNCRUDE GAS OIL - CATALYST 'A'



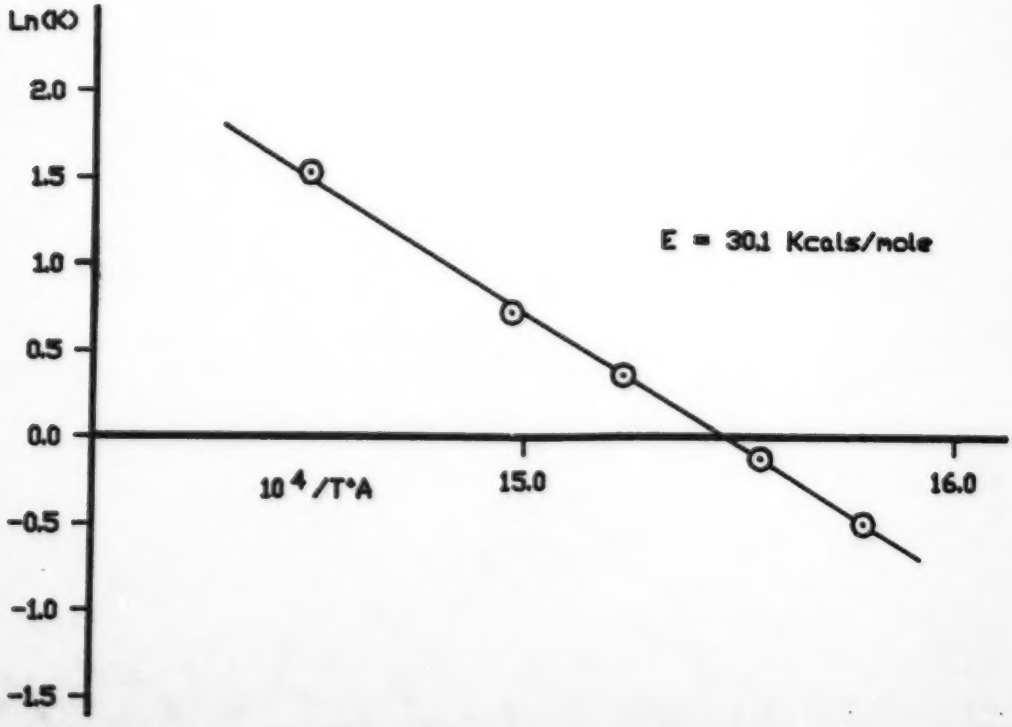
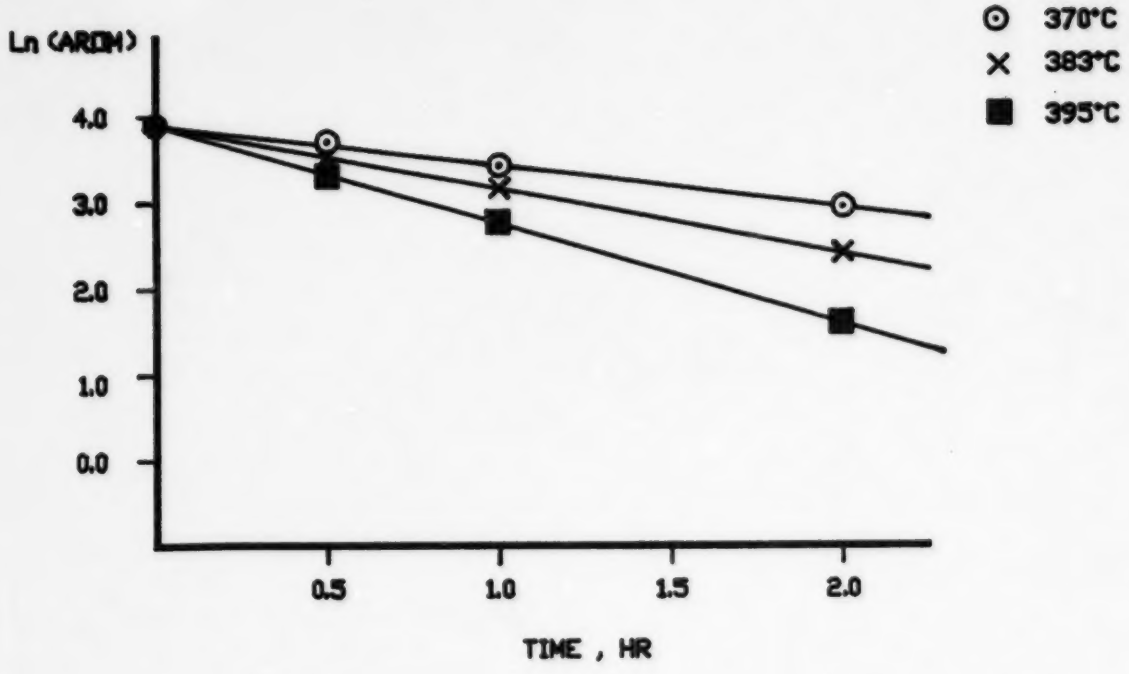


FIGURE 6

FIRST ORDER BEHAVIOUR FOR AROMATICS
AND GAS OIL REMOVAL FROM SYNCRUDE 315+ (SHELL 411)



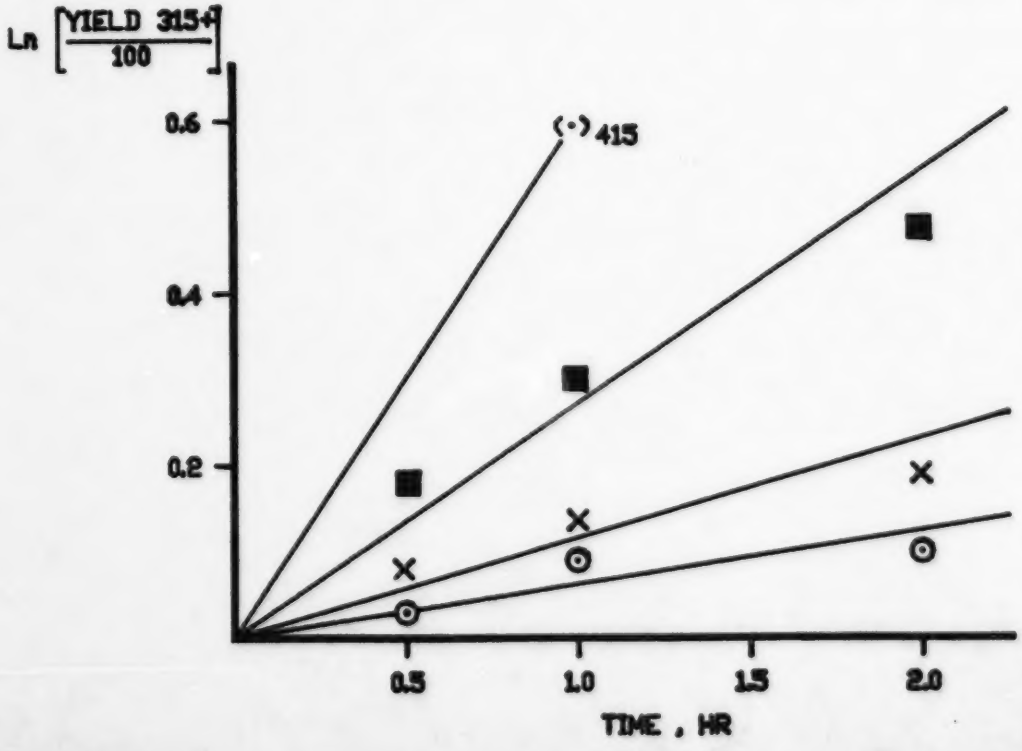


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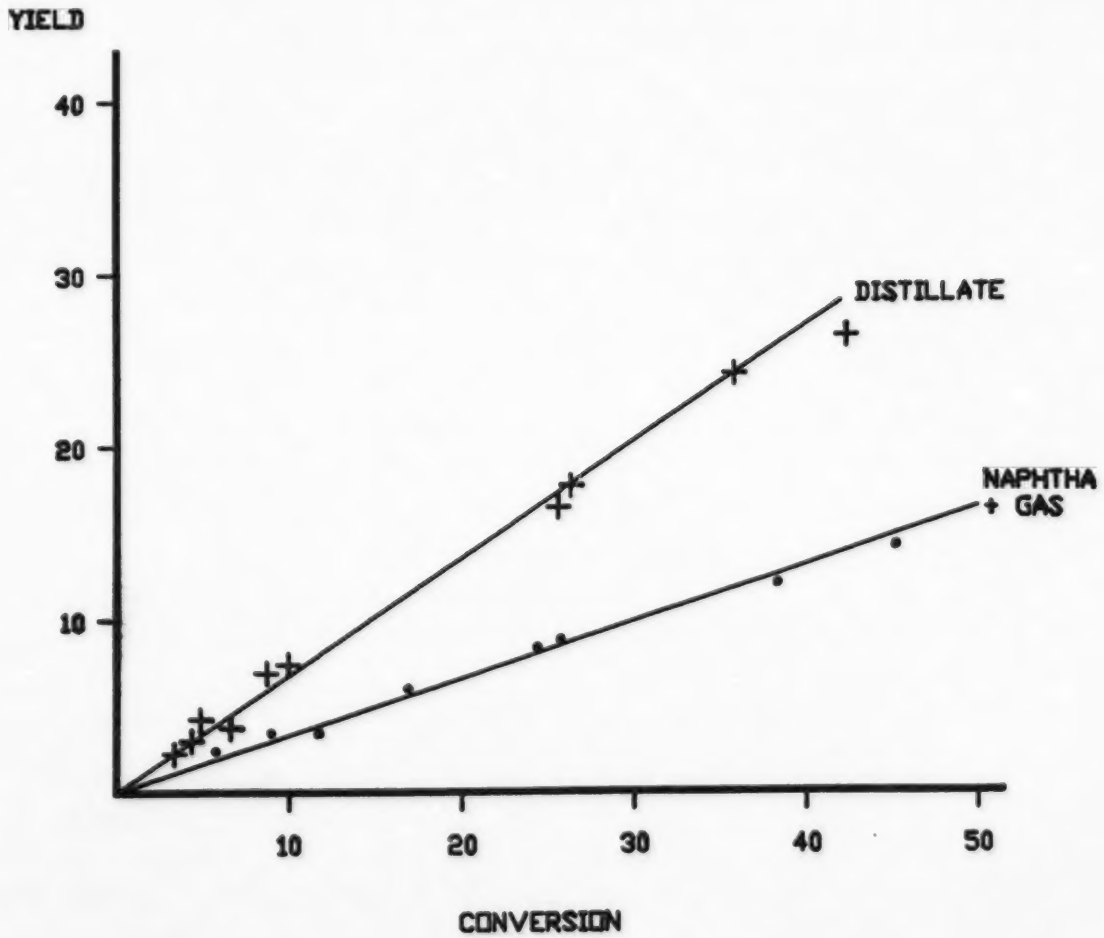
FIGURE 7

YIELDS OF DISTILLATE AND NAPHTHA + GAS
AS A FUNCTION OF CONVERSION : ALL DATA



APPENDIX B

CATALYST "A" - KINETIC RUN SEQUENTIAL ORDER

Run Order	Run #	Feed	LHSV (hr^{-1})	T (^{o}C)	P (psi)
1	4	SGO	2.0	395	2750
2	3	"	1.0	"	"
3	2	"	0.5	"	"
4	5	"	0.5	383	"
5	8	"	"	370	"
6	12	"	"	360	"
7	13	"	1.0	360	"
8	9	"	"	370	"
9	11	"	"	370	1500
10	6	"	"	383	2750
11	1	"	"	415	"
12	7	"	2.0	383	"
13	10	"	"	370	"
14	14	"	"	360	"
15	16	DSGO	2.0	360	"
16	10	"	"	370	"
17	7	"	"	383	"
18	4	"	"	395	"
19	3	"	1.0	395	"
20	1	"	"	415	"
21	6	"	"	383	"
22	11	"	"	370	1500
23	9	"	"	370	2750
24	15	"	"	360	"
25	14	"	0.5	360	"
26	8	"	"	370	"
27	5	"	"	383	"
28	2	"	"	395	"
29	12	NH_3 spiked DSGO	1.0	395	"
30	13	"	"	383	"

Note: Run # refer to those indicated in Tables 3 (DSGO) and 4 (SGO).

CATALYST SHELL 411 - KINETIC RUN SEQUENTIAL ORDER

Run Order	Run #	Feed	LHSV (hr^{-1})	T (^{o}C)	P (psi)
1	2	SGO	0.5	395	2750
2	3	"	1.0	"	"
3	4	"	2.0	"	"
4	7	"	2.0	383	"
5	6	"	1.0	"	"
6	5	"	0.5	"	"
7	8	"	0.5	370	"
8	9	"	1.0	"	"
9	10	"	2.0	"	"
10		"	2.0	360	"
11		"	1.0	"	"
12		"	0.5	"	"
13	11	"	1.0	370	1500
14	1	"	1.0	415	2750
15		DSGO	0.5	360	"
16		"	1.0	"	"
17		"	2.0	"	"
18	10	"	2.0	370	"
19	9	"	1.0	"	"
20	8	"	0.5	"	"
21	5	"	0.5	383	"
22	6	"	1.0	383	"
23	3	"	"	395	"
24	1	"	"	415	"
25	4	"	2.0	395	"
26	7	"	"	383	"
27	2	"	0.5	395	"
28	11	"	1.0	370	1500

Note: Run # refer to those indicated in Tables 5 (DSGO) and 6 (SGO).

CATALYST SHELL 753 - KINETIC RUN SEQUENTIAL ORDER

Run Order	Run #	Feed	LHSV (hr^{-1})	T (^{o}C)	P (psi)
1		SGO	2.0	395	2750
2		"	"	383	"
3		"	"	370	"
4	2	"	0.5	395	"
5	5	"	"	383	"
6	8	"	"	370	"
7	7	"	2.0	383	"
8	10	"	"	370	"
9	4	"	"	395	"
10	3	"	1.0	395	"
11	6	"	"	383	"
12	9	"	"	370	"
13		"	"	415	"
14	11	"	"	370	1500
15		DSGO	1.0	370	2750
16	2	"	0.5	395	"
17	5	"	"	383	"
18	8	"	"	370	"
19	10	"	2.0	370	"
20	7	"	"	383	"
21	4	"	"	395	"
22	3	"	1.0	395	"
23	6	"	"	383	"
24	11	"	"	370	1500

Note: Run # refer to those indicated in Tables 7 (DSGO) and 8 (SGO).

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